

Collection Oxidized MWCNTs as an Oxidizing Agent and Dopant in MWCNT@Polypyrrole Composite Formation**

Monika Wysocka-Żołopa,* Joanna Breczko, Emilia Grądzka, Anna Basa, Jakub Goclon, Alina Dubis, and Krzysztof Winkler^{*[a]}

Dedicated to Professor Marcin Opałło in recognition to his contribution to electrochemistry

A new approach to the formation of composites of carbon nanotubes and polypyrrole (PPy) is proposed. Oxidized multiwalled carbon nanotubes (ox-MWCNTs) are used as oxidation agents in pyrrole polymerization. The polymeric phase is deposited both at the surface of the carbon nanotube to form a core-shell structure and in the empty spaces of the MWCNT network. Each form of the polypyrrole phase exhibits different electrochemical properties. PPy deposited directly at the carbon nanotube surface as a uniform and dense layer is oxidized at less positive potentials, compared to the polymeric material deposited in the pores of the nanotube network. MWCNTs with anions incorporated into structural defects formed during their

1. Introduction

Polypyrrole (PPy) is one of the most frequently investigated conducting organic polymers in both basic and applied research. It exhibits many advantages, such as easy polymerization, good conductivity, a high rate of charge transfer, and charge storage capability, leading to many practical applications in biological and chemical sensors,^[1–3] charge storage devices,^[4–7] solar cells,^[8–11] and many others. Despite these advantages, PPy still suffers from a limiting cycling stability, a low permeability to supporting electrolyte counterions, and a low degree of oxidation. To overcome these critical problems and enhance the electrochemical performance of PPy, several strategies have been employed.

The application of nanostructured materials allows for a large electrochemical surface area and significantly improves the availability of polymeric materials for base electrolyte ions.^[12–15] Polymeric nanoparticles exhibit a low number of defects and high mechanical durability, and are also very useful in the production of flexible polymer electrodes.^[16–20]

In another strategy, nanocomposites of PPy and carbon nanomaterials, such as activated carbon,^[21-23] graphene oxide,^[24-28] reduced graphene oxide,^[29-31] and multi-walled^[32-36]

 [a] Dr. M. Wysocka-Żołopa, Dr. J. Breczko, Dr. E. Grądzka, Dr. A. Basa, Dr. J. Goclon, Dr. A. Dubis, Prof. K. Winkler Department of Chemistry University of Bialystok
 Ciolkowskiego 1 K, 15-245 Bialystok, Poland
 E-mail: monia@uwb.edu.pl winkler@uwb.edu.pl
 [**] MWCNT: Multi-walled carbon nanotubes

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oxidation in a piranha solution also act as dopants of the oxidized form of PPy. The polymeric film deposited directly at the ox-MWCNT surface is in its oxidized state. The redox processes involving this part of the PPy film are accompanied by the transport of cations of the supporting electrolyte. The charge transfer between ox-MWCNTs and the deposited PPy film is confirmed by the results of the theoretical calculations of the energy states at the carbon nanotube and polypyrrole interface. A neutral PPy film located in layers remote from the surface of the nanotube is oxidized at more positive potentials. The oxidation of PPy located in the pores of the ox-MWCNT network results in a broad voltammetric peak formation.

and single-walled^[37-40] carbon nanotubes, have been fabricated, and an improved performance of these composites in comparison to pristine PPy has been reported. Among these carbon nanomaterials, multi-walled carbon nanotubes (MWCNTs) are particularly useful in the preparation of composites with polypyrrole. They exhibit a good electrical conductivity, proper mechanical properties and a large effective surface area. They also form highly porous structures, enabling the efficient transport of ions into the electroactive layer. Composites of MWCNTs and PPy can be formed under electrochemical and chemical conditions. In electrochemical synthesis, PPy is electrodeposited at the surface of the electrode coated with a film of MWCNTs. In a typical chemical oxidative polymerization method of MWCNT/PPy composite formation, carbon nanotubes are dispersed in solution containing pyrrole and oxidation agents. Usually, ferric chloride, ferric perchlorate, hydrogen peroxide, and ammonium peroxidisulfate are used as oxidants for pyrrole polymerization.[41-44] Recently, Ramanavicius and co-workers[45] reported a new procedure for the conducting polymers formation by enzyme-assisted polymerization. Composites of polypyrrole and polyaniline with gold nanoparticles have been obtained using glucose oxidase as monomer oxidant. The electrochemical properties of the composites depend on the structure of the MWCNT layer,^[46-47] the morphology of the PPy film deposited at the surface of carbon nanotubes^[48-49] and the nature of doping ions incorporated into the polymeric structure during PPy formation.[49-50]

In the case of pure carbon nanotubes, their insolubility, poor dispersibility and poor compatibility with polymeric materials constitute significant problems in composite formation. Therefore, carbon nanotubes have been modified with functional groups in oxidation processes to enhance the



interaction between composite components.^[51-53] Common to carbon nanotube modification, carbon nanomaterials are oxidized by concentrated acids or acid mixtures, which results in the formation of hydroxyl-, carboxylic acid-, carbonyl-, and other oxygen-containing groups at the carbon nanotube surface.^[54-56] Such surface modification is also responsible for defect formation at the sidewalls.^[56] Organic dyads can also be used as dispersants for carbon nanotubes.^[57]

The proper polymer architecture at the surface of carbon nanotubes is another challenging issue in the process of PPy/ carbon nanotube composite formation. PPy tends to form an island-like, nonuniform layer on the surface of carbon nanotubes. Under these conditions, the control of the polymeric layer thickness is also challenging.

The structure and electronic properties of the polymeric component in PPy and carbon nanotube compositions are also influenced by the anionic dopants incorporated into the polymeric network during its formation to maintain composite electrical neutrality. Variations in the dopant anions can change the PPy conductivity by a few orders of magnitude.^[58] A large conductivity and stability of the PPy was achieved using large aromatic anionic dopants.^[59-66] Such large polycharged anionic dopants show limited movement during the charge-discharge process. In this case, cation transport is responsible for ion exchange during polymer-involved redox processes.^[59,65] Multiple-charged ionic dopants also form linkages between PPy chains and facilitate an interchain charge transfer.^[61] Zhitomirsky and co-workers doped PPy/carbon nanotube composites with various organic dyads.^[57,67-69] A significant increase in the electrical capacity and conductivity was observed. A similar effect was observed for PPy doped with surfactant nanocrystals.^[70] In this case, the dopant agent also acted as an oxidant.

Despite large progress achieved in the formation of composites containing carbon nanotubes and PPy, as well as the investigation of their structure and properties, there is a constant need to work on new methods of composite synthesis, leading to the production of materials showing a homogeneous surface coating of nanotubes with polymer and ensuring a high durability of the composite. Recently, Jang and co-workers^[71] demonstrated that graphene oxide can be used as a chemical oxidant in the formation of various conducting polymers, including PPy. They proposed a polymerization mechanism in which epoxy and hydroxyl groups present at the surface of oxidized graphene sheets initiate the polymerization process and the growth of the polymer chain on the graphene oxide surface. This research inspired the studies presented in this paper. This paper is focused on the application of oxidized MWCNTs (ox-MWCNTs) in the formation of composites composed of PPy and ox-MWCNTs. The ox-MWCNTs are used simultaneously as monomer oxidizers, doping agents of the formed polymer, and carbon components of the composite. The main attention is focused on the morphological studies of the created systems and determining the charge exchange mechanism during electrode processes, involving the polymer deposited on the surface of carbon nanotubes. The proposed procedure for composite synthesis allows for the formation of a uniform and homogeneous polymer layer on the ox-MWCNTs surface exhibiting unexpected and unique electrochemical properties.

2. Results

2.1 Composites of ox-MWCNTs and Polypyrrole

Composites of ox-MWCNTs and PPy were produced in a toluene solution containing a dispersion of ox-MWCNTs and pyrrole. The solvent was stirred during the polymerization process. Oxidized carbon nanostructures were then used both as monomer oxidation agents and as dopants. To exclude the possibility of pyrrole oxidation with light and oxygen, experiments were performed in the dark and in an argon atmosphere. The results of the investigation performed in the solution containing dispersed oxidized MWCNTs were also compared with the results of experiments conducted using pristine MWCNTs. In Figure 1, the morphology of the materials formed in solution containing pristine MWCNTs and ox-MWCNTs is shown. The experiment was conducted for the same polymerization time (24 hours). In the case of a solution containing pure MWCNTs and pyrrole, the polymer was not deposited at the surface of the MWCNTs (panel a of Figure 1). Panels b and c of Figure 1 show the morphology of the composite material formed in solution containing ox-MWCNTs and pyrrole. Two types of structures are formed in this case. The polymer is deposited on the surface of the ox-MWCNTs (spot 1 in Figure 1). The composite exhibits a core-shell structure, ox-MWCNT@PPy, and polypyrrole forms a relatively uniform layer on the surface of ox-MWCNTs. The thickness of the layer depends on the concentration of the monomer in solution. It can also be observed that the layers deposited in a solution containing a higher concentration of pyrrole are smoother and more uniform in thickness. The polymer is also formed in empty spaces of the carbon network, ox-MWCNT/PPy (spot 2 in Figure 1). In this case, PPy forms aggregates of spherical particles randomly distributed on the ox-MWCNT network.

The thickness of the polymer layer at the surface of the ox-MWCNTs can also be controlled by the time of pyrrole polymerization in the grown solution. In Figure 2, TEM images of composites containing ox-MWCNTs and polypyrrole formed for the same concentration of monomer in the solution are presented. Initially, polymer is deposited at the surface of carbon nanotubes. At longer polymerization times, the thickness of the polymer layer deposited at the surface of ox-MWCNTs increases, and spherical particles are formed. A linear relation between the thickness of the polypyrrole layer and the time of polymerization is shown in panel *d* of Figure 2.

Table 1 shows the results of the elemental analysis of the modified MWCNT nanomaterials. A mixture of MWCNTs and pyrrole was prepared in the same way as the composite of ox-MWCNTs and the PPy sample. The polymerization was conducted for 24 hours. For MWCNTs and ox-MWCNTs, the carbon content varies from 97% to 91%. For MWCNTs covered by a PPy shell, the presence of nitrogen was noted. The nitrogen





Figure 1. TEM images of the solid material obtained in 10 ml of toluene solution containing a) pyrrole (0.1 mol dm⁻³) and 2.5 mg of MWCNTs, b) pyrrole (0.1 mol dm⁻³) and 2.5 mg of ox-MWCNTs, c) pyrrole (0.2 mol dm⁻³) and 2.5 mg of ox-MWCNTs. Time of polymerization was 24 h. Spots (1) and (2) indicate two types of PPy structures deposited in the ox-MWCNTs network, ox-MWCNT@PPy and ox-MWCNT/PPy, respectively.

content amounts to 13.31% for materials formed in a toluene solution containing pyrrole and ox-MWCNTs. This value corresponds to ca. 60% of PPy in the composite material.

The material composition was also estimated via XPS analysis. Figure 3 shows the C 1s and O 1s XPS spectra obtained for oxidized carbon multi-walled carbon nanotubes. The C 1s spectrum (Figure 3a) demonstrates six components. Two pre-

dominant signals located at 283.61 eV and 284.51 eV are related to the carbon atoms in graphitic structures C=C (sp²) and C–C (sp³), respectively. The other four peaks are derived from C–O groups at 285.74 eV, C=O and C–O–C groups at 286.92 eV, O=C–O groups at 288.19 eV, and satellite peaks due to π - π * transitions at 290.1 eV.^[72–74] These oxygen functional groups were also found in the O 1s spectrum (Figure 3b). The signal at





Figure 2. TEM images of the composite obtained in toluene solution containing 0.1 mol dm^{-3} pyrrole and 0.25 mg cm^{-3} ox-MWCNTs. Time of polymerization was a) 2 h, b) 8 h, c) 24 h. d) Dependence of the thickness of the polymeric layer deposited at the surface of ox-MWCNTs on the time of polymerization.

531 eV derives from carbonyl, quinone, carboxyl or lactone groups, and the component at 532.61 eV corresponds to hydroxyl or ether groups.^[73–75] In the case of the ox-MWCNT and PPy composite, apart from functional groups characterized for oxidized carbon nanotube, functional groups derived from polypyrrole were also found. Figure 4a shows the C 1s XPS spectrum, where functional groups such as C=C (sp² carbon) at

284.3 eV, C–C (sp³ carbon) and C–N at 285.6 eV, C–O, C=O and C–O–C at 286.9 eV, C=O at 288 eV, O=C–O at 288.9 eV and satellite peaks due to π - π * transitions at 290.9 eV were detected. In comparison to the C 1s spectrum of ox-MWCNTs, an additional signal at 288 eV is observed. This signal corresponding to the C=O groups could be caused by the termination reaction and/or secondary reaction during the



Table 1. Elemental analysis of MWCNTs, ox-MWCNTs, a mixture of Py and MWCNTs and the PPy/ox-MWCNT composite.					
Material	Elemental analysis				
	C [%]	N [%]	H [%]		
MWCNTs	97.00	0	1.34		
ox-MWCNTs	91.10	0	3.70		
Py + MWCNTs	92.18	0	0.30		
PP and ox-MWCNT ^[a]	45.62	13.31	9.59		

[a] PPy and ox-MWCNT composite was synthesized for 24 hours in 10 ml of toluene solution containing 0.1 mol dm⁻³ pyrrole and 2.5 mg of MWCNTs



Figure 3. X-ray photoelectron spectra of ox-MWCNTs. The binding energy regions are a) C 1s and b) O 1s electrons.

polymerization process.^[72-74,76] The O 1s spectrum of the composite material (Figure 4b) is an image of this material obtained for pristine ox-MWCNTs. The additional confirmation of polypyrrole existence in the composite material is the N 1s spectrum (Figure 4c), which could be deconvoluted into three components, where the major peak component at a binding energy equal to 399.66 eV is assigned to neutral amine nitrogen (N–H). Two additional signals at 398.44 eV and 401.57 eV correspond to imine nitrogen (–N=) and positively charged nitrogen $(-N^+)$.^[72,73,77]

On the basis of a previous study, Raman spectra of MWCNTs provided valuable information on the existence of MWCNTs in a sample and the composition of carbon nanotubes. MWCNTs give rise to a graphite-like Raman spectrum with a prominent G-signal at approximately 1582 cm⁻¹. The so-called G-band,



Figure 4. X-ray photoelectron spectra of ox-MWCNTs and PPy composite. The binding energy regions are a) C 1s, b) O 1s and c) N 1s electrons.

which is a complex vibration parallel to the tube axis, may shift upon the presence of electron donors or acceptors. For samples with small crystal planar domains, a doublet structure may also be present.^[78,79]

There is also a D-band located at approximately 1347 cm⁻¹, resulting from defects in the nanotube lattice and originating from phonons. It was observed previously that the D-band is sensitive to the presence of disorder and defects within carbonaceous material. The intensity of the D-band is inversely proportional to the crystallite size La within the bulk material. It should be noted that the intensity of the D-band depends on the number of defects.^[80] A defect participates in the phonon scattering process, leading to the occurrence of a D Raman signal.^[81–83] Radial breathing modes typical of SWCNTs are not present in the Raman spectra of MWCNTs. This is due to restricted in-phase translation of carbon atoms in the radial direction.^[84]



Figure 5 shows the Raman and FT-IR spectra of MWCNTs (line b), ox-MWCNTs (line c), MWCNTs coated with PPy film formed through chemical oxidation of pyrrole (line d) and a composite of PPy and ox-MWCNTs (line e). The d line represents the spectrum of pristine MWCNTs after pyrrole treatment and may be considered a reference moiety. Functional groups that are attached to MWCNTs (sp²-base) can modify the nanotube network, leading to changes in their optical and electrical properties. It can be seen (Figure 5) that the D and G lines are broad and intense. The G peaks of ox-MWCNTs and the ox-MWCNT and PPy composite are upshifted slightly, compared with the G band of pristine MWCNTs. The D band of the PPY and ox-MWCNT composite (line e in Figure 5) is characterized by a dominant component at approximately 1357 cm⁻¹ with wide shoulders on the lower energy side. The observed phenomenon is connected with disorder-induced scattering of nanomaterials, such as functionalization or defects formed during a chemical transformation. This band is redshifted compared with the spectrum of pure MWCNTs. The dependence of the D-band intensity on the presence of defects was successfully used for evaluation of sample quality.^[85] The intensity ratio I_G/I_D for ox-MWCNTs and PPy composite is 1.31, while for MWCNTs and ox-MWCNTs it equals 0.75 and 0.71, respectively. It is worth noting that the lowest I_{c}/I_{D} ratio (0.71) was observed for ox-MWCNTs. This means that functionalization of the species analyzed here is the highest for ox-MWCNTs. The incorporation of PPy in the MWCNT network results in a decrease in the D band intensity and an increase in the I_{G}/I_{D} ratio. It seems that PPy could be successfully deposited via chemical polymerization onto a nanotube surface.

The lower panel of Figure 5 presents the IR spectrum of PPy. The intense band at 1560 cm^{-1} can be assigned to the C=C stretching in the pyrrole ring.^[86] The position of this band is influenced by the substituent connected to the pyrrole ring and the length of the PPy chains. It was observed that greater delocalization occurs for the longer polyconjugate system.^[87-89]



Figure 5. Raman and FT-IR spectra of a) PPy, b) MWCNTs, c) ox-MWCNTs, d) composite of pyrrole and MWCNTs, and e) composite of PPy and ox-MWCNTs.

The presence of two different polypyrrole structures in the deposit precipitated from the toluene solution containing pyrrole and ox-MWCNTs is also confirmed by the results of the thermogravimetric analysis (TGA). The curves of the relative mass versus temperature for the obtained composite are shown in Figure 6. For comparison, the thermogravimetric curve recorded for ox-MWCNTs and chemically produced PPy are shown. Carbon nanotubes are relatively stable in the studied temperature range (curve 1). The PPy is stable at approximately 220 °C (curve 2). Above these temperatures the polymeric phase decomposes. The small mass loss at approximately 100-180 °C is probably related to the removal of traces of water. In the case of composite, the decomposition of polypyrrole occurs in two temperature ranges (curve 3). In the temperature range from 220 to 320 °C, the first decomposition step is observed. Higher temperature decomposition of polypyrrole was still observed. However, the rate of decomposition at temperatures higher than ca. 320 °C is significantly lower than the rate of degradation at a lower temperature range. The shape of the thermogravimetric curve at temperatures higher than 320°C resembles the thermogravimetric curve recorded for chemically synthesized polypyrrole (curve 2 in Figure 6). These results indicate that two structurally different forms of polymers are formed by oxidizing pyrrole with ox-MWCNTs. Polypyrrole that decomposes in the shorter temperature range (220-320°C) shows a much more ordered and morphologically homogeneous structure. Core-shell, ox-MWCNT@PPy, structure is probably responsible for this thermal decomposition step.

2.2 Electrochemical Properties of ox-MWCNTs and Polypyrrole Composites

The electrochemical behavior of ox-MWCNT and PPy compo-

sites was compared with the voltammetric properties of PPy-

based materials obtained during typical chemical polymerization using Fe(III) ions as an oxidizing agent and under electrochemical conditions. The results of these studies are

100 90 80 70 Weight | % 60 ox-MWCNT/PP 50 ox-MWCNT@PP 40 30 20 0 200 400 600 800 Temperature / °C

Figure 6. TGA curves of (1) ox-MWCNTs, (2) pure chemically synthesized polypyrrole, and (3) ox-MWCNT and PPy nanocomposite.

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presented in Figure 7. The redox behavior of electrochemically formed polypyrrole is much more reversible than that of the material formed under chemical conditions. Chemically prepared polypyrrole was deposited at the electrode surface using the drop coating method. In this case, the voltammogram exhibits a poorly shaped polypyrrole oxidation peak at 0.52 V and a reduction peak at 0.45 V (voltammogram a in Figure 7). A high capacitance current is also observed at potentials less positive than the polypyrrole oxidation potential. At a more positive potential, a large oxidation peak O₂, corresponding to the polypyrrole overoxidation process, [90,91] is observed. Polymers that are chemically formed in solutions containing dispersed MWCNTs (MWCNT/PPy) are also oxidized at similar potentials (voltammogram b in Figure 7). The polymeric phase was deposited via pyrrole oxidation with Fe(III). In this case, a significant increase in both the capacitance current and faradaic current corresponding to polypyrrole-involved electrode processes is observed. Such behavior is related to the increase in the real surface area of the electroactive material due to the presence of the MWCNT component. The ratio of the polypyrrole oxidation current to the capacitance current increases compared to that observed for pure polypyrrole. A voltammogram c in Figure 7 shows the electrochemical properties of the ox-MWCNT and PPv composite formed by oxidation of pyrrole with oxidized MWCNTs. In this case, two additional voltammetric peaks, O3 and O4, are observed, exhibiting surface-like characteristics. At more positive potentials peak O₁ and peak O₂ are observed. In this panel, a voltammogram of a thin film of ox-MWCNTs is also presented (dashed line). In the studied range of potentials, no signals of the faradaic processes were observed.

The inset in Figure 7 shows the dependence of the logarithm of the oxidation current O_1 on the potential for the



Figure 7. Cyclic voltammograms of a) PPy formed in water containing 0.044 M pyrrole and 0.045 M FeCl₃, b) PPy formed in an aqueous dispersion of MWCNTs containing 0.044 M pyrrole and 0.045 M FeCl₃, and c) PPy formed in a toluene solution dispersion of ox-MWCNTs containing 0.1 M pyrrole. The broken line shows the voltammetric behavior of the ox-MWCNT film deposited at the surface of the Au electrode. The sweep rate was 0.1 V s⁻¹. The lower inset shows the dependence of the logarithm of the oxidation current on the potential for the initial 10% of the O₁ peak.

first 10% of the high oxidation peak. A slope of such a log *i*-*E* relation indicates the rate of the polymer oxidation process. These values show that the rate of oxidation of the polymer deposited at the surface of MWCNTs is much higher compared to the oxidation rate of the polymer deposited directly on the gold electrode surface.

The current of all polypyrrole oxidation peaks recorded for the ox-MWCNT and PPy composite increases with an increasing polymerization time. The results of the relevant experiment are shown in Figure 8. Initially, for polymerization times not exceeding approximately 10 hours, the voltammogram is dominated by the O₃ and O₄ peaks. The charge of the process occurring at the potentials of the O₁ peak is much lower than the charges corresponding to the Q₃ and O₄ peaks. Extending the polymerization time leads to the formation of a distinct O₁ peak. Finally, for long polymerization times in excess of approximately 20 hours, three well-developed peaks are observed in the voltammetric curves.

Another important feature of voltammograms recorded for the composite formed in a solution containing dispersed oxidized MWCNTs is the oxidation current recorded at an equilibration potential applied to the electrode before the positive potential of the voltammetric scan. Time of potential equilibration at -0.5 V influences the charge corresponding to the O₃ peak (Figure 9), and the charge corresponding to this peak increases with an increasing holding electrode time at the potential of equilibration. On the other hand, charges corresponding to O₁ and O₄ peaks are almost unaffected by the time of electrode holding at the initial potential. These results clearly indicate that the polymer form responsible for the presence of O₃ peaks on the voltammograms is formed as an oxidized material. Therefore, when a negative potential is applied, the polymer is reduced, and the oxidation current is recorded.

The voltammetric behavior of the ox-MWCNT and PPy composite is also significantly influenced by the nature of the supporting electrolyte. The voltammetric peaks O_1 and O_4 depend on the nature of supporting electrolyte anion. Peak O_3 , which appears at the less positive potentials, is influenced by



Figure 8. Cyclic voltammograms of ox-MWCNTs and PPy composite formed in solution containing 0.1 mol dm⁻³ pyrrole and 0.25 mg cm⁻³ ox-MWCNTs in toluene for a) 2 h, b) 8 h, c) 12 h, and d) 24 h. The sweep rate was 0.1 V s⁻¹.



Figure 9. Voltammograms of the ox-MWCNT and PPy composite recorded in a 0.1 M NaCl aqueous solution at 0.1 V s⁻¹. The holding electrode time at an initial potential of -0.5 V was a) 1, b) 5, and c) 10 seconds. The PPy/ox-MWCNT composite was then formed in a toluene solution containing 0.1 mol dm⁻³ pyrrole and 0.25 mg cm⁻³ ox-MWCNTs.

the cation of supporting electrolyte. In Figure 10, results of chronoamperometric investigations of the redox behavior of ox-MWCNT@PPy composite in solutions containing NaCl and KCl as a supporting electrolyte are presented Initially, the equilibrium potential of the composite/electrolyte interphase was determined under zero-current potentiometric conditions. The equilibrium potential obtained for a solution containing KCl as a supporting electrolyte is approximately 200 mV more positive than the equilibrium potential obtained in the NaCl solution (inset in Figure 10). This equilibrium potential was set as an initial potential in the chronoamperometric experiments. Next, a negative potential of -0.4 V was applied to the



Figure 10. Chronoamperometric curves of the ox-MWCNT@PPy composite recorded in an aqueous solution containing 1) 0.1 mol dm⁻³ NaCl, 2) 0.1 mol dm⁻³ KCl. The inset shows equilibrium potential of PPy/ox-MWCNT composite in (1) 0.1 mol dm⁻³ NaCl, (2) 0.1 mol dm⁻³ KCl.

electrode, and current-time transients were recorded. The charge corresponding to polymer reduction is much higher in a NaCl-containing solution compared to the reduction charge obtained in solution containing KCl as the supporting electrolyte. The changes in the charge corresponding to the constant potential polypyrrole reduction current correspond well to the changes in the charge related to the polypyrrole oxidation O_3 voltammetric peak in a solution containing different supporting electrolytes.

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In Figure 11, the voltammograms recorded at the electrode coated with the ox-MWCNT and PPy composite in a solution containing chlorides of different alkali metal cations are shown. The charges corresponding to O_1 , O_3 , and O_4 voltammetric peaks are summarized in Table 2. In the same table, the ionic and hydrated radii of the supporting electrolyte cations are summarized. The O_3 peak is strongly influenced by the nature of the supporting electrolyte cations. This peak was observed on voltammograms only in solutions containing small alkali metal and alkali earth metal cations (voltammograms 1 and 2). In the presence of larger cations in solution, the charge corresponding to the O_3 peak is much lower (voltammogram 3 in Figure 11) or is not observed at all in the voltammetric curves (voltammogram 4).



Figure 11. Voltammograms of the ox-MWCNT and PPy composite recorded in an aqueous solution containing (1) 0.1 mol dm⁻³ LiCl, (2) 0.1 mol dm⁻³ NaCl, (3) 0.1 mol dm⁻³ KCl, (4) 0.1 mol dm⁻³ RbCl at 0.1 Vs⁻¹. The PPy/ox-MWCNT composite was formed in a toluene solution containing 0.1 mol dm⁻³ pyrrole and 0.25 mg cm⁻³ ox-MWCNTs.

Table 2. Correlation between ionic radius of selected supporting electro-lyte cations and oxidation charge corresponding to the O_3 peak.					
lon	Crystal ionic radius ^[a] [Å]	Stokes radius ^[a] [Å]	Hydrated radius ^[a] [Å]	Charge corresponding to O3 peak [μC]	
Li+	0.60	2.38	3.82	1.40	
Na ⁺	0.95	1.84	3.58	1.33	
K ⁺	1.33	1.25	3.51	~0.25	
Rb ⁺	1.48	1.18	3.29	_	
Mg ²⁺	0.65	3.47	4.28	1.23	
Ca ²⁺	0.99	3.10	4.12	1.31	
Ba ²⁺	1.36	2.90	4.04	-	
Et_4N^+	4.00	2.82	4.00	-	
[a] From Ref. [92]					



Similar results were obtained in solutions containing chlorides of alkali earth metal cations (Figure 12). In the case of smaller cations, such as Mg^{2+} or Ca $^{2+}$, all three peaks (O₁, O₃, and O_4) are observed in voltammograms. In a solution containing larger Ba^{2+} cations, peak O_3 is not recorded. This peak was also absent in voltammograms recorded in a solution containing large tera(alkil)ammonium cations. In Figure 12, a voltammogram recorded in a solution containing tetra(ethyl) ammonium chloride (Et₄NCI) as a supporting electrolyte is shown. It can be expected that reducing the size of the doping ion during polymer layer charging should favor the oxidation process. It is also worth emphasizing that the changes in the charge corresponding to the O₁ peak correlate very well with the crystal ionic radius of the tested cations. However, no dependence of this charge on the size of the solvated ion was observed (Table 2).

3. Discussion

Oxidized MWCNTs can be used as oxidant agents for the initiation of the pyrrole polymerization process. The IR, Raman spectroscopy and XPS spectra indicate that the surface of the MWCNTs is modified with -OH, -COOH, and C-O-C groups during oxidation with H_2SO_4 and H_2O_2 . Epoxy groups have oxidizing properties and can oxidize pyrrole to radicals, which can initiate the polymerization process. The polymeric material that is formed in this process exhibits two kinds of morphologies. A compact polypyrrole layer is deposited on the surface of ox-MWCNTs, and less ordered structures are formed in the gaps between the nanotubes. They have limited contact with the carbon material.

The structure of the polymeric material deposited within the ox-MWCNT network influences its redox properties. The PPy that is formed in the open spaces between ox-MWCNTs (ox-MWCN/PPy) is oxidized at potentials more positive than ca. 0.45 V. On voltammograms, the broad peak O_1 is related to this



Figure 12. Voltammograms of the PPy/ox-MWCNT composite recorded in an aqueous solution containing (1) 0.1 mol dm⁻³ MgCl₂, (2) 0.1 mol dm⁻³ CaCl₂, (3) 0.1 mol dm⁻³ BaCl₂, and (4) 0.1 mol dm⁻³ (Et)₄NCl at 0.1 V s⁻¹. The PPy/ox-MWCNT composite was formed in a toluene solution containing 0.1 mol dm⁻³ pyrrole and 0.25 mg cm⁻³ ox-MWCNTs.

redox process. This process resembles the electrochemical oxidation of PPy, which is formed under typical chemical conditions in solutions containing MWCNTs, pyrrole and FeCl₃ as oxidation agents. The oxidation of PPy is accompanied by the transport of anions from the solution to the polymeric phase.

More complex behavior is observed for the compact polymeric layer deposited at the surface of ox-MWCNTs (ox-MWCNT@PPy). Both voltammetric peaks related to the oxidation of the formed PPy layer exhibit surface-like characteristics. The O₃ peak, which appears at potentials close to 0.1 V depends on the nature of the cation present in the solution. The process responsible for peak O₄, which is recorded in a more anodic potential range, is related to the transport of supporting electrolyte anions. It should also be emphasized that the reproducibility of the results related to the O₃ peak is rather low, especially if the conditions for the oxidation of nanotubes or their purification after the oxidation process slightly change. It was also observed that long-term washing of the nanotubes led to a significant reduction in the height of the O_3 peak or its complete disappearance. Replacing oxygenated carbon nanotubes in 2 mol dm⁻³ of an H₂SO₄ solution, their rewashing with distilled water and their use as pyrrole oxidizing agents leads to the formation of a polymer on their surface showing electrochemical activity in the range of peak O₃ (Figure 13). The results of this experiment clearly suggest that SO₄²⁻ ions participate in the process occurring within the potential range of O₃ peaks on voltammograms. A similar experiment involving treating nanotubes with 2 moldm⁻³ sulfuric acid does not lead to the formation of a product that can oxidize pyrrole and form a polymer. It can thus be concluded that sulfate ions adsorbed at the defective sites in multi-walled carbon nanotubes are responsible for the electrode processes occurring in the potential range of the O_3 peak. The presence of these SO_4^{2-} ions at the surface of ox-MWCNTs can also explain the formation of an oxidized inner layer of PPy directly deposited on the surface of the nanotubes. In this case, SO_4^{2-} ions act as counterions for the oxidized PPy layer.

The results of electrochemical experiments correlate well with the theoretical calculations of the energy level distribution near the Fermi level in the mixed PPy and ox-MWCNT system. The introduction of defects combined with functional groups in the pristine semiconducting SWCNTs strongly modified their electronic properties.^[93] Defects typically introduce new states in the original band gap, while functional groups introduce new states to the whole electronic structure. Consequently, the Fermi level is moved to lower energies. Therefore, the electronic properties of such oxidized nanotubes are different than those of pristine nanotubes. In our mixed system, the mutual interaction is driven by van der Waals forces and π - π stacking interactions. The shortest distances between the carbon and nitrogen atoms from the adsorbed PPy and the carbon atoms from ox-SWCNT(10,0) are in the range of 3.4–3.6 Å. Therefore, the electronic properties of the oxidized carbon nanotubes should unambiguously determine the properties of the entire system. Figure 14 shows the total and projected DOS for the PPy/ox-SWCNT(10,0) system calculated at the DFT(PBE) + D3(BJ) Articles doi.org/10.1002/celc.202100566





Figure 13. Graphic presentation of the experimental results of SO_4^{-2} ion incorporation into the ox-MWCNT structure and their influence on the redox behavior of ox-MWCNT and PPy composite.

level of theory. The polymer exhibited metallic properties, where the unoccupied bands just above the Fermi level corresponded to those of the HOMO state of the isolated PPY^[94] combined with the carbon states of the nanotube. Figure 14 also shows the plot of the charge density for these empty states (0–0.1 eV). The next unoccupied bands were located in the range of 0.2 to 0.7 eV above the Fermi level for the majority and minority spin states originating from ox-SWCNTs(10,0). Therefore, the electron transfer between PPy and ox-MWCNTs results in oxidation of the polymer. Such behavior explains the oxidized state of the polypyrrole inner layer located on the surface of carbon nanotubes. Electronic interactions between the polymer and the carbon material are also responsible for the significant shift of the redox potential of the PPy inner layer toward less positive potentials.

The electrode processes of the PPy layer deposited at the surface of ox-MWCNTs are schematically described in Figure 15.

This paper is the beginning of a new research area on the use of oxidized carbon nanomaterials in the formation of composites with conductive polymers, without the need for an oxidant to initiate the polymerization process. The procedure described in this paper can be successfully applied to the formation of composites of carbon nanotubes, and other p-dopable conductive polymers, such as polyaniline, polythiophene and their derivatives. Many aspects related to the material described in this paper require additional detailed research. Much attention was required to develop a synthesis method that led to the production of only carbon nanotube structures covered with a polymer layer, ox-MWCNT@PPy. The influence of the oxidation conditions of carbon nanotubes on the polymerization process should also be the subject of



PPY/ox-SWCNT(10,0)



Figure 14. Total and projected density of states (DOS) for PPy/ox-SWCNT(10,0) calculated at the DFT(PBE) + D3(BJ) level (left). The charge density of the unoccupied band is indicated by an asterisk (right). The yellow surface represents an isovalue of 10^{-3} e/Bohr. Nitrogen atoms are blue, oxygen atoms are red, hydrogen atoms are white, and for transparency, carbon atoms in PPy are green, while those in the nanotube are black.

detailed studies. A major goal of future research will also be focused on the formation of mechanically stable composites that exhibit good electronic conductivity and a high electrical capacitance. These and a number of other issues will be the subject of future studies on the use of oxidized carbon nanotubes in the formation of composites with polypyrrole and other conductive polymers.

The synthesized material can have a number of potential applications. The electrode processes of studied composites involve transport of both cations and anions of supporting electrolyte. Therefore such composites can be applied as an electroactive materials for ion-sensing. Their use in the selective determination of alkaline and alkaline-earth cations seems to be of particular interest. Recently, application of composites based on conducting polymers and carbon nanostructures for heavy metal sensing has been reviewed.^[95] Such composites could also be used as electroactive materials in supercapacitors^[96-99] and electrocatalysts in biologically-active compounds determination.^[100–102]

4. Conclusions

Oxidized multi-walled carbon nanotubes can be used as both oxidants and dopants for the formation of ox-MWCNTs and PPy composites. The epoxide groups present at the ox-MWCNTs are probably responsible for oxidation of the monomer and initiation of the polymerization process. In the composite formation process, two types of PPy domains are formed: (i) carbon nanotubes are coated by the uniform layer of PPy, and (ii) PPY aggregates are also formed in the pores of the ox-MWCNT network. Such a composite structure results in complex redox behavior. The polypyrrole phase deposited directly at the surface of ox-MWCNTs is oxidized at less positive potentials than PPy, which is formed in the empty spaces of the carbon nanotube network.

An inner layer of PPy is deposited at the ox-MWCNT surface in the form of a positively charged film. The positive charge of the polymer phase is compensated by the anions adsorbed in the defects of carbon nanotubes, which are formed during carbon nanomaterial oxidation in a piranha solution. Due to the limitations in the mobility of these ions, the electrode processes associated with this polymer layer are conducted with the participation of cation transport of the base electrolyte. In the presence of large-sized base electrolyte cations, the charge exchange processes involving this layer are limited. Theoretical calculations of the energy level distribution at the ox-MWCNTs and PPY interphase show the possibility of a charge exchange between two phases. The neutral PPy layers farther from the surface of the carbon nanotubes are oxidized at more positive potentials. This process is accompanied by the transport of supporting electrolyte anions. The electronic interaction between ox-MWCNTs and the PPy layer located close to the carbon nanotube surface, and confirmed by the results of theoretical calculations, is responsible for the significant shift of PPy oxidation toward less positive potentials (peak O₃).

Finally, at the most positive potentials, the PPy agglomerates located between the ox-MWCNTs are oxidized. At





Reduction of the MWCNT@polypyrrole

Figure 15. Schematic representation of the ox-MWCNT@PPy composite involved charge transfer processes.

voltammograms, this process results in the formation of a broad peak typical for other systems frequently reported for composites of MWCNTs and PPy.

The method developed in this investigation can be used for the fabrication of other composites containing MWCNTs and organic, conducting polymers.

Experimental Section

Chemicals: MWCNTs, pyrrole, FeCl₃ and anhydrous toluene (99.9%) (Sigma-Aldrich Chemical Co.), were used as received. Sulfuric acid (96%) and hydrogen peroxide (30%) from POCh were used in the MWCNT oxidation process. The supporting electrolytes for the electrochemical measurements LiCl, LiClO₄, NaCl, RbCl, MgCl₂, CaCl₂, BaCl₂, and (C₂H₅)₄NClO₄ were used as received from Sigma-Aldrich

Chemical Co. Pure deionized water with a resistivity of 18.2 $M\Omega\text{-}cm$ was obtained from Milli-Q/Millipore Systems.

Apparatus: The Raman spectra of solid MWCNTs, ox-MWCNTs, composites of PPy and ox-MWCNTs, and a mixture of Py and MWCNTs were recorded in backscattering geometry within the spectral range from 150 to 3000 cm⁻¹ with a resolution better than 1 cm⁻¹ using an inVia Raman Microscope Renishaw equipped with a liquid-nitrogen-cooled CCD RenCAM detector. The excitation line $\lambda_{ext} = 514$ nm was used, and the power of the laser energy was kept below 2 mW to avoid the thermal and photochemical degradation of the sample.

FT-IR spectra were obtained using a Thermo Scientific Nicolet 6700 FT-IR spectrometer in the spectral range from 4000 to 500 cm^{-1} with a spectral resolution of 2 cm⁻¹. The spectra were measured in transmittance mode as KBr pellets.

The elemental composition of the investigated nanomaterials was determined using a Vario Micro Cube CHNS elemental analyzer, Germany. Conditions for the elemental analysis for the carbon, hydrogen, and nitrogen contents were as follows: reaction tube packed of copper wires and tungstic oxide; SS column, 2 m long, internal diameter of 6 mm; temperature of the combustion tube 1150 °C, temperature of the reduction tube 850 °C; gases: helium (flow rate – 200 ml/min), oxygen (flow – 200 ml/min). The weight of sample used was 2–2.5 mg. To determine the content of C, H, and N elements in the samples, calibration was conducted using a sulfanilamide standard.

Voltammetric experiments were performed on an AUTOLAB Model 283 Potentiostat/Galvanostat (EG&G Princeton Applied Research, Oak Ridge, TN, USA) with a three-electrode cell. The AUTOLAB system was controlled with GPES 4.9 software by the same manufacturer. A gold disc electrode with a diameter of 1.5 mm (Bioanalytical Systems Inc., West Lafayette, IN, USA) was used as the working electrode. Prior to each experiment, the electrode was washed with acetone and dried. An Ag/AgCl/saturated KCI electrode was then separated from the working electrode using a ceramic tip (Bioanalytical Systems Inc.). The counter electrode was a platinum tab with an area of approximately 0.5 cm².

TEM images were obtained using a Tecnai G2 20 X-TWIN microscope (FEI Company, Hillsboro, Oregon, USA) with an LaB6 emitter and an HAADF detector operating at 120/200 kV. For energy dispersive X-ray fluorescence measurements, an EDX instrument and Ametek software (Berwyn, Pennsylvania, USA) were used. This software facilitates standardless quantification of atomic weight and atomic percentage. The accelerating voltage for the electron beam was 20 kV, and the working distance was 10 mm.

Thermogravimetric analysis (TGA) was performed using a Mettler Toledo Star TGA/DSC system. Nitrogen was used as the purge gas (0.1 dm³min⁻¹). Samples weighing 2 mg were placed in aluminum pans and heated from 50 °C to 1000 °C at a heating rate of $10 \,^{\circ}$ C min⁻¹.

X-ray photoelectron spectroscopic (XPS) measurements were performed using a PHI 5000 VersaProbe (ULVAC-PHI) spectrometer with monochromatic Al K α radiation (hv = 1486.6 eV) from an X-ray source operating at a 100 μ m spot size, 25 W and 15 kV. Highresolution (HR) XPS spectra were then collected with a hemispherical analyzer at a pass energy of 117.4 eV and an energy step size of 0.1 eV. The X-ray beam was incident at the sample surface at an angle of 45° with respect to the surface normal, and the analyzer axis was located at 45° with respect to the surface. Casa XPS software was then used to evaluate the XPS data. Deconvolution of all HR XPS spectra was performed using a Shirley background and a Gaussian peak shape with a 30% Lorentzian character.

Oxidation of MWCNTs: The oxidation of MWCNT was performed according to the procedure described in the literature.^[54] Then, 300 mg of MWCNTs was added to 25 ml of the piranha solution $(H_2SO_4;H_2O_2 \text{ in a ratio of 7:3})$, and the dispersion was kept for 5 h at room temperature. The obtained solution was diluted in deionized water and filtered. The resulting product was washed three times with deionized water and dried in an oven at 40 °C. Oxidized MWCNTs form dispersion in water which are stable for about 2 h. After this time, agglomeration of carbonaceous material and precipitation of ox-MWCNTs from the solution is observed.

Synthesis of ox-MWCNTs and PPv composites: The ox-MWCNTs and PPy composite was prepared via chemical polymerization of 0.1 mol dm⁻³ pyrrole in 10 ml deoxygenated toluene containing a dispersion of 2.5 mg ox-MWCNTs. The carbon nanotube component acts both as an oxidizing agent and as a dopant. The solution was stirred while the synthesis was conducted. Argon was bubbled through the solution at all times during the synthesis. The dark deposit precipitated from the solution was filtered, washed with the solvent used in the synthesis and dried at 90 °C for 24 h. For the electrochemical measurements, the proper amount of ox-MWCNTs and PPy composite powder (1.0 mg cm⁻³) was dispersed via sonication in a dichloromethane solution to form a homogenous mixture. Twenty microliters of this solution were dropped on the surface of the Au electrode, and the solvent was evaporated. The electrode was then placed in a water solution containing a supporting electrolyte, and voltammetric experiments were performed. Prior to the electrochemistry experiments, the solution was deoxygenated via bubbling with argon for 10 min.

Computational methods: The computational approach was based on a pseudopotential plane-wave method using PWSCF code as is implemented in the QUANTUM ESPRESSO package.^[103] We used the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional,^[104] taking spin polarization into account for all the calculations. In addition, Grimme's D3(BJ) dispersion corrections with the Becke-Johnson damping function^[105] were used to account for the van der Waals interactions. The Vanderbilt ultrasoft pseudopotential method was used to approximate the ion-electron interaction.^[106] The Kohn-Sham orbitals were expanded using plane waves with a cutoff for the wave functions of 30 Ry and a cutoff for the charge density of 200 Ry. All the structures were fully relaxed using the Broyden-Fletcher-Goldfarb-Shanno (BFGS) quasi-Newton algorithm until the forces on each atom were less than 0.01eV/Å.^[107] The total energy was minimized using Hellman-Feynman forces. Integrals over the Brillouin zone were computed using a 1×1×4 Monkhorst-Pack^[108] k-point mesh. For density of states (DOS) calculations, we increased the density of the k-point mesh to $1 \times 1 \times 10$. In addition, the peak width for broadening was set to 0.05 eV for better visualization of the DOS.

Periodic boundary conditions and a supercell approximation were applied to model the PPy interactions with the surface of oxidized defective carbon nanotubes. An initial optimized supercell representing SWCNT(10,0) containing 200 carbon atoms (five unit cells) with lengths of 21.42 Å was used to study the mixed system. The most important issue in the modeling of PPY/ox-SWCNT(10,0) was the mutual matching of the two components to maintain periodicity. By taking three unit cells of the optimized pyrrole dimer (3 d_{PPY} is 21.52 Å^[94]), we obtained a very good lattice match.

In the next step, we introduced nanotube surface functional groups based on the relative concentration of these groups based on the deconvolution of the high-resolution C 1s XPS signal, namely, two



hydroxyl, one carbonyl and one carboxyl groups. Since the experimental data concerns oxidized MWCNTs of unknown structures, we were not able to determine the relative ratio of C:O in our ox-SWCNT(10,0) system. Considering that the functional groups mainly exist in the defect sites (or at the edges), we introduced two single carbon vacancies to the bare carbon nanotube at some distance. Our previous calculations revealed that the position in which a COOH group is attached to a defective SWCNT is of primary importance;¹⁹³ therefore, both the carboxyl group and oxygen from the carbonyl group were located in the most stable position of the unsaturated two-coordinated C site. Then we placed the PPY chain on the surface of the carbon nanotubes to maximize the π - π stacking interactions.

All figures were produced using the visualization programs $\mathsf{VESTA}^{(109)}$ and XcrySDen. $^{(110)}$

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Conflict of Interest

The authors declare no conflict of interest.

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- [1] T. F. Otero, S. Beaumont, Sens. Actuators B 2017, 253, 958–966.
- [2] M. Xue, F. Li, D. Chen, Z. Yang, X. Wang, J. Ji, Adv. Mater. 2016, 28, 8265–8270.
- [3] A. Nezhadali, L. Mehri, R. Shadmehri, Sens. Actuators B 2012, 171–172, 1125–1131.
- [4] L. Yuan, B. Yao, B. Hu, K. Huo, W. Chen, J. Zhou, Enegy Environ. Sci. 2013, 6, 470–476.
- [5] M. S. Kim, J. H. Moon, P. J. Yoo, J. H. Park, J. Electrochem. Soc. 2012, 159, A1052-A1056.
- [6] D. P. Dubal, Z. Caban-Huertas, R. Holze, P. Gomez-Romero, *Electrochim. Acta* 2016, 191, 346–354.
- [7] Y. Huang, J. Tao, W. Meng, M. Zhu, Y. Huang, Y. Fu, Y. Gao, C. Zhi, Nano Energy 2015, 11, 518–525.
- [8] S. S. Jeon, C. Kim, J. Ko, S. S. Im, J. Mater. Chem. 2011, 21, 8146-8151.
- [9] L. Y. Chang, C. T. Li, Y. Y. Li, C. P. Lee, M. H. Yeh, K. C. Ho, J. J. Lin, *Electrochim. Acta* 2015, 155, 263–271.
- [10] J. Xu, M. Li, L. Wu, Y. Sun, L. Zhu, S. Gu, L. Liu, Z. Bai, D. Fang, W. Xu, J. Power Sources 2014, 257, 230–236.
- [11] N. Sangiorgi, A. Sangiorgi, F. Tarterini, A. Sanson, *Electrochim. Acta* 2019, 305, 322–328.
- [12] J. H. Chang, C. R. Aleman de Leon, I. W. Hunter, *Langmuir* 2012, 28, 4805–4810.
- [13] I. Rawal, A. Kaur, Sensor Actuat. A-Phys. 2013, 203, 92–102.
- [14] E. Jaworska, A. Kisiel, A. Michalska, K. Maksymiuk, *Electroanalysis* 2018, 30, 716–726.

- [15] S. S. Shinde, G. S. Gund, D. P. Dubal, S. B. Jambure, C. D. Lokhande, *Electrochim. Acta* 2014, 119, 1–10.
- [16] Y. Shi, L. Pan, B. Liu, Y. Wang, Y. Cui, Z. Bao, G. Yu, J. Mater. Chem. A 2014, 2, 6086–6091.
- [17] M. Zhu, Y. Huang, Q. Deng, J. Zhou, Z. Pei, Q. Xue, Y. Huang, Z. Wang, H. Li, Q. Huang, C. Zhi, Adv. Energy Mater. 2016, 6, 1600969.
- [18] L. Tong, M. Gao, C. Jiang, K. Cai, J. Mater. Chem. A 2019, 7, 10751– 10760.
- [19] L. Zhu, L. Wu, Y. Sun, M. Li, J. Xu, Z. Bai, G. Liang, L. Liu, D. Fang, W. Xu, RSC Adv. 2014, 4, 6261–6266.
- [20] Q. Xu, C. Wei, L. Fan, W. Rao, W. Xu, H. Liang, J. Xu, Appl. Surf. Sci. 2018, 460, 84–91.
- [21] L. Yang, Z. Shi, W. Yang, Electrochim. Acta 2015, 153, 76-82.
- [22] A. Porjazoska Kujundziski, D. Chamovska, M. Cvetkovska, T. Grchev, Int. J. Electrochem. Sci. 2012, 7, 4099–4113.
- [23] S. Khan, A. Majid, R. Raza, J. Mater. Sci. Mater. Electron. 2020, 31, 13597–13609.
- [24] S. Konwer, R. Boruah, S. K. Dolui, J. Electron. Mater. 2011, 40, 2248–2255.
- [25] B. Rikhari, S. P. Mani, N. Rajendran, J. Mater. Sci. 2020, 55, 5211-5229.
- [26] Z. Lv, Y. Chen, H. Wei, F. Li, Y. Hu, C. Wei, C. Feng, *Electrochim. Acta* 2013, 111, 366–373.
- [27] J. Xue, Q. Sun, Y. Zhang, W. Mao, F. Li, C. Yin, ACS Omega 2020, 5, 10995–11004.
- [28] C. Bora, S. K. Dolui, Polymer 2012, 53, 923-932.
- [29] V. Chandra, K. S. Kim, Chem. Commun. 2011, 47, 3942–3944.
- [30] T. Qian, C. Yu, S. Wu, J. Shen, J. Mater. Chem. A 2013, 1, 6539–6542.
 [31] A. Wang, T. Qian, C. Yu, S. Wu, J. Shen, Appl. Phys. A 2015, 120, 693–
- 698. [32] Y. Chen, J. Li, L. Tan, Q. Li, X. Zhang, H. Xu, *Electrochim. Acta* **2017**, *258*,
- 43–50.
- [33] S. Dhibar, S. Sahoo, C. K. Das, J. Appl. Polym. Sci. 2013, 130, 554–562.
- [34] P. Gemeiner, J. Kulicek, M. Mikula, M. Hatala, L. Svorc, L. Hlavata, M. Micusik, M. Omastova, Synth. Met. 2015, 210, 323–331.
- [35] A. A. lurchenkova, E. O. Federovskaya, I. P. Asanov, V. E. Arkhipov, K. M. Popov, K. I. Baskakova, A. V. Okotrub, *Electrochim. Acta* 2020, 335, 135700.
- [36] J. Park, N. Raseda, E. S. Oh, K. Ryu, J. Appl. Polym. Sci. 2016, 133, 43307.
- [37] K. H. An, K. K. Jeon, J. K. Heo, S. C. Lim, D. J. Bae, Y. H. Lee, J. Electrochem. Soc. 2002, 149, A1058-A1062.
- [38] K. H. An, S. Y. Jeong, H. R. Hwang, Y. H. Lee, Adv. Mater. 2004, 16, 1005–1009.
- [39] J. Wang, Y. Xu, X. Chen, X. Sun, Compos. Sci. Technol. 2007, 67, 2981– 2985.
- [40] J. Wang, K. Cai, S. Shen, J. Yin, Synth. Met. 2014, 195, 132–136.
- [41] A. Kausaite-Minkstimiene, V. Mazeiko, A. Ramanaviciene, A. Ramanavicius, *Colloids Surf. A* 2015, 483, 224–231.
- [42] K. Nishio, M. Fujimoto, O. Ando, H. Ono, T. Murayma, J. Appl. Electrochem. 1996, 26, 425–429.
- [43] H. K. Chitte, N. V. Bhat, A. V. Gore, G. N. Shind, Materials Sciences and Applications 2011, 2, 1491–1498.
- [44] K. Leonavicius, A. Ramanaviciene, A. Ramanavicius, *Langmuir* 2011, 17, 10970–10976.
- [45] N. German, A. Ramanaviciene, A. Ramanavicius, *Polymer* **2020**, *12*, 3026.
- [46] Y. Yesi, I. Shown, A. Gnguly, T. T. Ngo, L. C. Chen, K. H. Chen, *ChemSusChem* 2016, 9, 370–378.
- [47] X. Sun, Y. Xu, J. Wang, J. Solid State Electrochem. 2012, 16, 1781-1789.
- [48] X. Liu, L. Xue, Y. Lu, Y. Xia, Q. Li, J. Electroanal. Chem. 2020, 862, 114006.
- [49] J. Kulicek, P. Gemeiner, M. Omastova, M. Micusik, Chem. Pap. 2018, 72, 1651–1667.
- [50] Y. Zhu, K. Shi, I. Zhitomirsky, J. Mater. Chem. A 2014, 2, 14666-14673.
- [51] Y. Chen, B. Lin, X. Zhang, J. Wang, C. Lai, Y. Sun, Y. Liu, H. Yang, J. Mater. Chem. A 2014, 2, 14118–14126.
- [52] S. M. Yuen, C. C. M. Ma, C. L. Chiang, J. A. Chang, S. W. Huang, S. C. Chen, C. Y. Chuang, C. C. Yang, M. H. Wei, *Composites Part A* 2007, 38, 2527–2535.
- [53] A. A. Koval'chuk, V. G. Shevchenko, A. N. Shchegolikhin, P. M. Nedorezova, A. N. Klyamkina, A. M. Aladyshev, *Macromolecules* 2008, 41, 7536–7542.
- [54] V. Datsyuk, M. Kalyva, K. Papagelis, J. Parthenios, D. Tasis, A. Siokou, I. Kallitsis, C. Galiotis, *Carbon* 2008, 46, 833–840.
- [55] Z. Qu, G. Wang, J. Nanosci. Nanotechnol. 2012, 1, 105-111.
- [56] N. Sezer, M. Koc, Surface Interfaces 2019, 14, 1–8.



- [57] K. Shi, I. Zhitomirsky, J. Mater. Chem. A 2013, 1, 11614–11622.
- [58] P. C. Wang, J. Y. Yu, React. Funct. Polym. 2012, 72, 311–316.
- [59] X. M. Lang, Q. Y. Wan, C. H. Feng, X. J. Yue, W. D. Xu, S. S. Fan, Synth. Met. 2010, 160, 1800–1804.
- [60] E. Hakansson, T. Lin, H. Wang, A. Kaynak, Synth. Met. 2006, 156, 1194– 1202.
- [61] B. Weng, R. Shephard, J. Chen, G. G. Wallace, J. Mater. Chem. 2011, 21, 1918–1924.
- [62] R. K. Sharma, A. Karakoti, S. Seal, L. Zhai, J. Power Sources 2010, 195, 1256–1262.
- [63] I. Carrillo, E. S. de la Blanca, M. I. Redondo, M. V. Garcia, M. J. Gonzalez-Tejera, J. L. G. Fierro, E. Enciso, Synth. Met. 2012, 162, 136–142.
- [64] D. K. Ariyanayagamkumarappa, I. Zhitomirsky, Synth. Met. 2012, 162, 868–872.
- [65] C. H. Feng, P. C. H. Chan, I. M. Husing, *Electrochem. Commun.* 2007, 9, 89.
- [66] X. Li, I. Zhitomirsky, J. Power Sources 2013, 221, 49-56.
- [67] S. Chen, I. Zhitomirsky, Mater. Lett. 2014, 135, 47-50.
- [68] Y. Shu, K. Shi, I. Zhitomirsky, J. Power Sources 2014, 268, 233–239.
- [69] S. Chen, I. Zhitomirsky, Mater. Manuf. Processes 2016, 31, 1246-1252.
- [70] K. Shi, I. Zhitomirsky, ACS Appl. Mater. Interfaces 2013, 5, 13161–13170.
- [71] M. Kim, C. Lee, Y. D. Seo, S. Cho, J. Kim, G. Lee, Y. K. Kim, J. Jang, Chem. Mater. 2015, 27, 6238–6248.
- [72] S. Gomez, N. M. Rendtorff, E. F. Aglietti, Y. Sakka, G. Suarez, Chem. Phys. Lett. 2017, 689, 135–141.
- [73] NIST X-ray Photoelectron Spectroscopy Database 20, Version 4.1: http://srdata.nist.gov/xps/.
- [74] G. Beamson, D. Briggs, *High Resolution XPS of organic polymers* The Scienta ESCA300 Database, John Willey and Sons Ltd., Chichester, 1992.
- [75] F. G. Pacheco, A. A. C. Cotta, H. F. Gorgulho, A. P. Santos, W. A. A. Macedo, C. A. Furtado, *Appl. Surf. Sci.* 2015, 357, 1015–1023.
- [76] J. Cao, Y. Wang, J. Chen, X. Li, F. C. Walsh, J. H. Ouyang, D. Jia, Y. Zhou, J. Mater. Chem. A 2015, 3, 14445–14457.
- [77] C. Malitesta, I. Losito, L. Sabbatini, P. G. Zambonin, J. Electron Spectrosc. Relat. Phenom. 1995, 76, 629–634.
- [78] F. Tuinstra, J. L. Koenig, J. Chem. Phys. 1970, 53, 1126.
- [79] R. J. Nemanich, G. Lucovsky, S. A. Solin, Mater. Sci. Eng. 1977, 31, 157.
- [80] L. G. Cancado, K. Takai, T. Enoki, M. Endo, Y. A. Kim, H. Mizusaki, A. Jorio, L. N. Coelho, R. Magalhaes-Paniango, M. A. Pimenta, *Appl. Phys. Lett.* 2006, *88*, 163106.
- [81] D. B. Schuepfer, F. Badaczewski, J. M. Guerra-Castro, D. M. Hofmann, Ch. Heiliger, B. Smarsly, P. J. Klar, *Carbon* 2020, 161, 2020, 359–372.
- [82] V. Meunier, A. G. S. Filho, E. B. Barros, M. S. Dresselhaus, *Rev. Mod. Phys.* 2016, *88*, 025005.
- [83] R. Beams, L. G. Canado, L. Novotny, J. Phys. Condens. Matter. 2015, 27, 083002.
- [84] P. Rai, D. R. Mohapatra, K. S. Hazra, D. S. Misra, J. Ghatak, P. V. Satyam, Chem. Phys. Lett. 2008, 455, 83.
- [85] J. F. Rodriguez-Nieva, E. B. Barros, R. Saito, M. S. Dresselhaus, *Phys. Rev. B* 2014, 90, 235410.

- [86] J. W. Kim, F. Liu, H. J. Choi, S. H. Hong, J. Joo, *Polymer* 2003, 44, 289–293.
- [87] A. T. Dubis, S. J. Grabowski, J. Phys. Chem. 2003, 107, 8723-8729.
- [88] A. Mizera, S. J. Grabowski, P. Ławniczak, M. Wysocka-Żołopa, A. T. Dubis, A. Łapiński, *Polymer* 2019, 164, 142–153.
- [89] J. Tabačiarová, M. Mičušik, P. Fedorko, M. Omastowá, Polym. Degrad. Stab. 2015, 120, 392–401.
- [90] J. B. Schlenoff, H. Xu, J. Electrochem. Soc. 1992, 139, 2397-2401.
- [91] P. Novok, B. Rosch, W. Vielstich, J. Electrochem. Soc. 1991, 138, 3300– 3304.
- [92] E. R. Nightingale Jr., J. Phys. Chem. 1959, 63, 1381-1387.
- [93] J. Goclon, M. Kozlowska, P. Rodziewicz, ChemPhysChem 2015, 16, 2775–2782.
- [94] J. Goclon, K. Winkler, Chem. Select 2018, 3, 373–383.
- [95] M. A. Deshmukh, M. D. Shirsat, A. Ramanaviciene, A. Ramanavicius, Critical Rev. Anal. Chem. 2018, 48, 293–304.
- [96] A. Afzal, F. A. Abuilaiwi, A. Habib, M. Awais, S. B. Waje, M. A. Atieh, J. Power Sources 2017, 352, 174–186.
- [97] B. Gnana, S. Raja, T. H. Koa, J. Acharyaa, M. K. Seoc, M. S. Khilb, H. Y. Kima, B. S. Kim, *Electrochim. Acta* 2020, 334, 135627.
- [98] S. Wang, Y. Liang, W. Zhuo, H. Lei, M. S. Javed, B. Liu, Z. Wang, W. Mai, Mater. Chem. Front. 2021, 5, 1324–1329.
- [99] J. P. Jyothibasu, M. Z. Chen, R. H. Lee, ACS Omega 2020, 5, 6441–6451.
 [100] Q. Zengab, J. Chen, F. Gaob, X. Tu, Y. Qian, Y. Yu, L. Lu, W. Wang, Synth. Met. 2021, 271, 116620.
- [101] D. Maity, R. T. Rajendra Kumar, *Biosens. Bioelectron.* **2019**, *130*, 307–314.
- [102] E. Zor, Y. Oztekin, A. Ramanaviciene, Z. Anusevicius, H. Bingol, J. Barkauskas, M. Ersoz, A. Ramanavicius, J. Electrochem. Soc. 2014, 161, H3064-H3069.
- [103] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L. Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, R. M. Wentzcovitch, J. Phys. Condens. Matter. 2009, 21, 395502.
- [104] S. Gimme, S. Ehrlich, L. Goerigk, J. Comb. Chem. 2011, 32, 1456-1465.
- [105] G. Beamson, D. Briggs, High Resolution XPS of organic polymers The Scienta ESCA300 Database, John Willey and Sons Ltd., Chichester, 1992.
- [106] D. Vanderbilt, Phys. Rev. B 1990, 41, 7892-7895.
- [107] R. Fletcher, Practical methods of optimization, Wiley, Chichester, 2008.
- [108] H. J. Monkhorstand, J. D. Pack, Phys. Rev. B 1976, 13, 5188-5192.
- [109] K. Momma, F. Izumi, J. Appl. Crystallogr. 2011, 44, 1272-1276.
- [110] A. Kokalj, J. Molec. Graph. Model. 1999, 17, 176–179.

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ARTICLES

Oxidized multi-walled carbon

nanotubes are used as oxidation agents in pyrrole polymerization. The polymeric phase is deposited both at the surface of the carbon nanotube to form a core-shell structure and in the empty spaces of the multi-walled carbon nanotubes network. The charge transfer between multi-walled carbon nanotubes and the deposited polypyrrole film influences the composite-involved redox processes.



Dr. M. Wysocka-Żołopa*, Dr. J. Breczko, Dr. E. Grądzka, Dr. A. Basa, Dr. J. Goclon, Dr. A. Dubis, Prof. K. Winkler*

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Oxidized MWCNTs as an Oxidizing Agent and Dopant in MWCNT@Polypyrrole Composite Formation

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