Composites of unmodified or oxidized carbon nano-onions (CNOs/ox-CNOs) with poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) are prepared with different compositions. By varying the ratio of PEDOT:PSS relative to CNOs, CNO/PEDOT:PSS composites with various PEDOT:PSS loadings are obtained and the corresponding film properties are studied as a function of the polymer. X-ray photoelectron spectroscopy characterization is performed for pristine and ox-CNO samples. The composites are characterized by scanning and transmission electron microscopy and differential scanning calorimetry studies. The electrochemical properties of the nanocomposites are determined and compared. Doping the composites with carbon nanostructures significantly increases their mechanical and electrochemical stabilities. A comparison of the results shows that CNOs dispersed in the polymer matrices increase the capacitance of the CNO/PEDOT:PSS and ox-CNO/PEDOT:PSS composites.

1. Introduction

The unique physical properties of nanomaterials have placed them at the forefront of emerging technologies. Significant enhancement of electrical, optical, mechanical, and structural properties is commonly found for novel nanomaterials. Carbon nanostructure materials are potentially useful in energy storage and conversion devices due to their favorable mechanical and electrical properties.\(^{[1]}\) A lot of attention has been paid to the capacitive properties of thin films of carbon nanotubes (CNTs)\(^{[2]}\) and of graphene\(^{[3]}\) due to their porous structures and large surface areas. These materials exhibit properties of typical double-layer capacitors, in which energy storage arises mainly from the separation of electronic and ionic charges at the interfaces between the electrode materials and the electrolytes in solution.

Carbon nano-onions (CNOs) are one of the ideal platforms for the preparation of new materials due to their unique physicochemical properties. Recently, the electrochemical properties of thin films formed from small CNOs (5–6 nm in diameter, six to eight fullerene shells) were investigated.\(^{[4]}\) They show high chemical stability and large specific surface area.\(^{[5]}\) The noncovalent and covalent functionalization of CNOs changes their physicochemical properties.\(^{[6]}\) The integration of CNOs with polymers,\(^{[7]}\) biomolecules,\(^{[8]}\) or polyelectrolytes\(^{[9]}\) has led to the development of new hybrid materials and sensors. CNOs have a variety of potential applications, including optical limiting,\(^{[10]}\) field emission in solar cells,\(^{[11]}\) fuel cell electrodes,\(^{[12]}\) charge storage devices,\(^{[13]}\) and hyperlubricants.\(^{[14]}\)

Composite materials based on the integration of carbon structures with substances can lead to materials possessing properties of the individual components. The development of composites for use as supercapacitor electrodes can provide enhanced potential electronic and ionic conductivity, and can considerably improve charge storage and delivery. Their pseudocapacitive behavior has been studied extensively owing to their high power capability, long cycle lifetime, and fast charge and discharge rates. Materials used for such purposes include carbon materials,\(^{[15]}\) conducting polymers,\(^{[16]}\) and metal oxide nanoparticles.\(^{[17]}\)

The use of poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS) as a viable electrode material due to its conjugated backbone and processing ability has been reported.\(^{[18]}\) PEDOT:PSS has a conjugated backbone that allows good transport of delocalized electrons through the \(\pi\)-orbital systems.\(^{[19]}\) Combining a relatively high conductivity with optical transparency in the doped state, it is suitable for applications such as electrodes in light-emitting diodes,\(^{[20]}\) transistors,\(^{[21]}\) photovoltaics,\(^{[22]}\) sensors,\(^{[23]}\) ion-selective electrodes,\(^{[24]}\) electrochromic devices,\(^{[25]}\) polymer electrolyte fuel cells,\(^{[26]}\) and high power-density supercapacitors.\(^{[27]}\) Recently, several strategies have been applied to increase the conductivity of PEDOT:PSS. It has been reported that incorporation of carbon nanostructures, such as CNTs\(^{[28]}\) or graphene,\(^{[29]}\) into conventional conducting polymers improves their conductivity. Increased con-
ductivities have been achieved by doping with polyoxometalate,[30] metal particles,[31] inert solvents such as sorbitol,[32] mannitol,[32] dimethyl sulfoxide,[33] and tetrahydrofuran,[34] or polymers.[35]

Composite films of CNTs and PEDOT:PSS were prepared via electrochemical co-deposition from solutions containing CNTs and the corresponding monomer or by chemical methods. Carbon nanostructures acted as both the backbone of the three-dimensional micro- and nanoporous structures and the effective charge balancing dopant within the polymer. All the composites showed improved mechanical integrity, higher electronic and ionic conductivity, and exhibited larger electrode specific capacitance. In addition, the CNT/PEDOT:PSS nanocomposites (50 wt % PEDOT) had a specific capacitance of 198.2 F g\(^{-1}\) and a capacitance degradation of 26.9 % after 2000 cycles, much better than those of pristine PEDOT and CNTs/PEDOT (50 wt % PEDOT).[36] For example, Lota et al. have revealed that the CNTs/PEDOT nanocomposite electrode can exhibit excellent electrochemical performance when operating in acidic, alkaline, and organic media.[37] Frackowiak et al. reported multiwalled CNT and PEDOT:PSS composites that achieved capacitance values of 100 F g\(^{-1}\).[38] Similarly, excellent mechanical and electrochemical stability was observed for graphene oxide and PEDOT:PSS composites, which exhibit capacitance values of 108 F g\(^{-1}\).[39]

The challenge is the fabrication of composite materials containing conducting polymers and carbon material with the right ratio of the two components and a homogeneous structure. To address this, we synthesized novel composites including CNO particles and PEDOT:PSS. The advantage of small CNOs over CNTs, or bigger CNOs, is their easier dispersion in aqueous solutions, which improves the homogeneity of the composites. X-ray photoelectron spectroscopy (XPS) studies revealed oxygen-containing groups on the CNO surface. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) characterization of the synthesized composites showed good dispersion of CNO particles throughout the polymer matrix. Differential scanning calorimetry (DSC) thermograms of the composites confirmed the presence of the PEDOT:PSS layer on the carbon nanostructure’s surface. Therefore, the electrochemical properties, especially the capacitive properties, of the composites were investigated.

2. Results and Discussion

2.1. XPS Characterization of Oxidized CNOs

We performed XPS studies to confirm the presence of oxygen-containing functional groups on the CNOs’ surface, which were oxidized in HNO\(_3\) solution. Figure 1 presents the XPS C 1s spectra of oxidized (top) and reference (pristine; bottom) CNO samples. The measured curves are presented as solid lines. For both samples the main C 1s peak was unsymmetric, which is characteristic of conducting forms of carbon (for example, graphite).[40] For the reference sample (CNO) the main C 1s peak could be fitted with four components centered at 285.2, 285.6, 287.8, and 291.0 eV. The first two peaks were assigned to sp\(^2\) and sp\(^3\) hybridized carbon atoms, respectively.[41] The other two peaks were interpreted as relaxation shake-up peaks,[42] as no oxygen or other elements (except the gold substrate) were observed in the survey spectrum (not shown). For the HNO\(_3\)-oxidized sample (ox-CNO) a prominent signal (~4 % versus 96 % carbon signal) appeared in the O 1s region (Figure 2). The C 1s peak obtained for this sample could be fitted with six components: 285.2, 285.6, 287.4, 288.4, 291, 287.8.

![Figure 1. XPS C 1s spectra of modified (top) and reference (bottom) CNOs.](image1)

![Figure 2. XPS O 1s spectrum of modified CNOs.](image2)
and 295.5 eV. The first two peaks were again assigned to sp² and sp³ carbon atoms. The integrated intensity of the 285.2 eV peak dropped (by ≈5%) relative to the reference sample (pristine CNO), which we assigned to carbon–carbon bonds breaking and bonding to oxygen-containing functional groups. The broad signal at 287.4 eV could arise from carbon atoms bound to oxygen in the form of oxygen bridges –C=O– or carbonyl groups >C=O.[43] The 288.4 and 291.5 eV peaks could arise from carboxyl O=C=O groups, while the 295.5 eV peak could arise from adsorbed CO and/or CO₂.[44] Note that all the peaks >286 eV were superimposed by satellite peaks. The survey spectrum obtained for this sample (not shown) gave no evidence for the presence of nitrogen (N 1s) or other elements except carbon, gold, and oxygen; thus, the presence of nitrogen-containing functional groups on the surface of ox-CNOs was excluded. The O 1s spectrum could be fitted with three peaks centered at 531.6, 533.4, and 536.6 eV. The 531.6 eV peak could arise from carbonyl groups >C=O,[45] with some possible contribution of oxygen from carboxyl O=C=OH groups.[46] The 533.4 eV peak could also arise from carboxyl groups (as these groups contain two differently bound oxygen species) and from oxygen bridges -C=O–.[43] The 536.6 eV peak was assigned to adsorbed O₂, H₂O,[45] CO, and CO₂.[46] The 533.4 eV peak could also potentially arise from hydroxyl –OH groups;[45] however, this was excluded as no corresponding carbon peak (C 1s component centered around 286.4–286.9 eV) was observed in the recorded XPS spectra.[43,45,47] The results confirmed modification of CNOs by attachment of oxygen-containing functional groups. The data are consistent with our previous findings by Boehm titration methods, which suggested the presence of carboxyl groups on the surface of HNO₃-oxidized CNOs.[47]

2.2. Morphology Characterization and Colorimetric Studies of the ox-CNO/PEDOT:PSS and CNO/PEDOT:PSS Composites

Electrochemical capacitors based on carbon electrodes are of two types: electrical double layer capacitors and supercapacitors.[46] The capacitance values are strictly correlated with the nature and surface of the electrode/electrolyte interface. Generally, the more developed the specific surface the higher the charge accumulation.[49]

The PEDOT:PSS and CNO nanocomposites were obtained via noncovalent modification of the carbon nanostructures with polymer layers. Solutions were prepared by dispersing CNOs or ox-CNOs in the PEDOT:PSS solution in water using ultrasonication without any oxidation process. The morphology and roughness of the synthesized CNO composites were studied by SEM, and the results for ox-CNO/PEDOT:PSS and CNO/PEDOT:PSS films are shown in Figure 3. The morphology of the composites differs significantly from the morphology of thin films formed only by the filler, PEDOT:PSS. At the micrometer scale, PEDOT:PSS forms smooth and uniform layers on the gold surface (Figure 3 a). The morphology of the CNO/PEDOT:PSS films was highly dependent on the concentration of the polymer in the composites. The CNO/PEDOT:PSS composites with
very low concentration of PEDOT:PSS (1:0.1 mass ratio; Figure 3b) exhibit porous morphologies with many channels and outcroppings. The roughness of the composite surface decreases with increasing amounts of PEDOT:PSS on the CNO surface (Figure 3b–e).

Composites prepared using ox-CNOs were also obtained. SEM studies did not show significant differences between the structures of the composites prepared from unmodified and oxidized CNOs. The TEM images in Figure 4 clearly reveal PEDOT:PSS polymer wrapping of CNO and show a significant increase of PEDOT:PSS in the composite. Increasing the concentration of PEDOT:PSS copolymer during the synthesis (see Figure 4a, b) resulted in the formation of island-like structures of the composite (structures 1 and 2 in Figure 4b). Homogeneous structures were obtained for low concentrations of PEDOT:PSS in the composite of about 10% (Figure 4a, structure 1). Required characteristics of carbon materials for electrochemical applications include mainly wettability and high conductivity. Wettability is generally improved by the presence of surface functionalities, whereas electrical conductivity depends mainly on the microstructures.[10] The nanotextural properties of carbon are characterized by its specific surface area, the presence of micro- and mesopores, and their shapes. High surface area is required for high-performance supercapacitors. These microstructural variations have a profound influence on the resulting capacitive behavior of the CNO/PEDOT:PSS composites.

Analysis of the pure components of the composite (CNOs and PEDOT:PSS), and the CNO/PEDOT:PSS and ox-CNO/PEDOT:PSS derivatives was performed to determine the presence of polymer in the composite structures. DSC thermograms of the composites are presented in Figure 5. A curve with a broad melting peak with a minimum around 50–70 °C was observed, due to solvent.[51] Weak endotherms were observed between 320 and 450 °C, ascribed to the presence of the polymer layer on the carbon nanostructure’s surface. The degradation peak at 320 °C is due to the decomposition of PSS via rupture of the sulfonate groups from the styrene.[52] The melting peak around 450 °C is due to another PEDOT/PSS polymer backbone decomposition. These results also indicate that the CNO/PEDOT:PSS nanocomposite is fairly stable up to a temperature of around 300 °C and subsequently starts to decompose, whereas pristine PEDOT:PSS copolymer undergoes decomposition in the temperature range of 200–300 °C.[53] As shown in Figure 5, the DSC curves clearly showed that the mass of PEDOT:PSS increased in the composites (see curves b–e) and confirmed the presence of the PEDOT:PSS layer on the carbon nanostructure’s surface.

2.3. Voltammetric Study of the CNO/PEDOT:PSS and ox-CNO/PEDOT:PSS Composites

The electrochemical characteristics of CNO/PEDOT:PSS were investigated and correlated with the nature of the CNO surface, microtextural characterization, and the composition of films. To elucidate the effect of the unmodified and oxidized CNO structures on the electrochemical properties of the PEDOT:PSS composites, cyclic voltammetric studies were performed. Solid films of ox-CNO/PEDOT:PSS and CNO/PEDOT:PSS were prepared by drop coating. The carbon nanostructure composites (3 mg mL−1) were sonicated in ethanol solution. A drop of solution containing the dispersed functionalized carbon nanostructures was then deposited on the electrode surface. After sol-
vent evaporation, the electrode covered with a thin film of modified carbon nanostructures was transferred to an aqueous solution containing 0.1 mol L\(^{-1}\) NaCl as the supporting electrolyte.

The voltammetric responses of ox-CNO/PEDOT:PSS and CNO/PEDOT:PSS (1:1 mass ratio) were compared with those of the references, namely pristine CNO and PEDOT:PSS (see Figure 6). All voltammograms exhibit pseudorectangular pro-
The specific capacitance, $C_s$, of the electrode can be estimated from the cyclic voltammetry curves by using Equation (1):

$$C_s = \frac{\int_{E_1}^{E_2} i(E)dE}{2vm(E_2 - E_1)}$$

where $E_1$ and $E_2$ are the cutoff potentials in cyclic voltammetry, $i(E)$ is the instantaneous current, $i(E)dE$ is the total voltammetric charge obtained by integration of the positive and negative sweeps in the cyclic voltammograms, $v$ is the scan rate, and $m$ is the mass of the individual sample. The specific capacitances of PEDOT, CNOs, CNO/PE-DOT:PSS, and ox-CNO/PE-DOT:PSS composite electrodes were calculated using Equation (1), and the values are collected in Table 1.

The specific capacitance can also be calculated by Equation (2):

$$i_c = C_s vm$$

where $i_c$ is the capacitive current, $m$ is the mass of material deposited on the electrode surface, and $v$ is the potential sweep rate. Figure 8 shows the voltammetric behavior at different sweep rates. The capacitive current varies linearly with the sweep rate at 300 mV versus Ag/AgCl for all concentrations of PEDOT:PSS in the composite (Figure 8, curves a–d). A linear dependence of the capacitive current on the sweep rate is observed over a large sweep rate range (up to 300 mVs$^{-1}$), as shown in Figure 8e.

The values of the specific capacitances calculated using Equation (2) from the dependence of the current on the scan rate for the different compositions are collected in Table 1. The values of the specific capacitances obtained by integration of $I$–$E$ curves and those calculated from the linear relationship of $I$–$v$ plots are in good agreement. In both cases, the capacitance of the films is controlled by the amount of CNO in the composites. CNOs improve the composite film properties by making them more active for faradaic reactions, and conferring larger specific capacitances and better stabilities than for pristine PE-DOT:PSS.

3. Conclusions

Our studies show that uniform PEDOT:PSS layers were successfully adsorbed on CNO surfaces. Two main parameters, the amount of CNOs in the composites and the porosity of the material, influence the capacitance of the systems. The PEDOT:PSS polymer network and CNO structures significantly increase the roughness and specific surface area of the nano-

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Figure 8. Cyclic voltammograms of GC electrodes covered with CNOs/PEDOT:PSS; the mass ratio of CNOs to PEDOT:PSS was: a) 1:0.1, b) 1:0.25, c) 1:0.5, and d) 1:1, in 0.1 mol L$^{-1}$ NaCl. The sweep rate was 1) 5, 2) 10, 3) 20, 4) 50, 5) 75, 6) 100, 7) 150, 8) 200, 9) 250, and 10) 300 mV s$^{-1}$. e) Dependence of the capacitive current on the sweep rate for CNOs/PEDOT:PSS at +300 mV in 0.1 mol L$^{-1}$ NaCl. The mass ratio of CNOs to PEDOT:PSS was: (●) 1:0.1, (●) 1:0.25, (▲) 1:0.5, and (●) 1:1.
composite electrodes. The electrochemical data of the composites showed a specific capacitance of about 96 F g⁻¹ for CNOs/PEDOT:PSS (1:1 mass ratio). The simple synthesis of these materials, their cation-exchange properties, and their facile electrochemistry make them attractive for applications as electrodes for supercapacitors.

**Experimental Section**

Materials: All chemicals and solvents used were commercially available and used without further purification: poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS; Aldrich Company, 1.3 wt% dispersion in H₂O, conductive grade), nitric acid (Aldrich Company), sodium chloride (POCH Company). Aqueous solutions were prepared with deionized water with a resistivity of 18.4 MΩ from Millipore.

Small CNOs were obtained by annealing nanodiamond powder (Mo+o, 5 nm average particle size) under a positive pressure of helium at 1650 °C for 1 h. After separation and purification, the CNOs were heated at 200 °C to remove the residue from the carbon surface. High-resolution TEM images of the CNOs were reported elsewhere. The mixture was then centrifuged for 10 min and the black powder collected in the bottom of the test tube was washed several times with 0.1 M NaOH and deionized water and dried overnight in a vacuum oven (7 = 120 °C) to yield ox-CNOs.

Crude six- to eight-shell CNOs (20 mg) were dispersed by ultrasonication for 30 min and refluxed for 3 h in 3.0 mL of aluminia and 0.25 mL diamond polish (Metadi II, Buehler). The electrode was then sonicated in water to remove traces of alumina from the metal surface, washed with water, and dried. The counter electrode was made from platinum mesh (0.25 mm) and was cleaned by heating in a flame for approximately 30 s. A silver wire immersed in 0.1 M AgCl and separated from the working electrode by a ceramic tip (Bioanalytical Systems Inc.) served as the reference electrode.

The studied films were imaged by secondary electron SEM with the use of an S-3000N scanning electron microscope from FEI (Tokyo, Japan). The accelerating voltage of the electron beam was either 15 or 20 keV and the working distance was 10 mm. TEM images were recorded using the FEI Tecnai instrument. The accelerating voltage of the electron beam was 200 keV.

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**Keywords:** carbon · composites · electrochemistry · nanostructures · polymers

A Mettler DSC system with STAR® analysis software was used to conduct DSC experiments. The thermal curve from the calorimeter was used to evaluate the thermal properties of the materials. The following measuring parameters were used: surrounding atmosphere: nitrogen; heating rate: + 10 °C·min⁻¹.

Voltammetric experiments were performed using a potentiostat/galvanostat model AUTOLAB (Utrecht, The Netherlands) with a three-electrode cell. Electrochemical impedance spectroscopy (EIS) measurements were performed on an AUTOLAB (Utrecht, The Netherlands) computerized electrochemistry system equipped with a PGSTAT 12 potentiostat and frequency response analyzer (FRA) expansion card with a three-electrode cell. The AUTOLAB system was controlled with the GEPES 4.9 software of the same manufacturer.

A glassy carbon (GC) disk with a diameter of 1.6 mm (Bioanalytical Systems Inc.) was used as the working electrode. The surface of the electrode was polished using extra-fine carbonundum paper (Buehler) followed by 0.3 μm alumina and 0.25 μm diamond polishing compound (Metadi II, Buehler). The electrode was then sonicated in water to remove traces of alumina from the metal surface, washed with water, and dried. The counter electrode was made from platinum mesh (0.25 mm) and was cleaned by heating in a flame for approximately 30 s. A silver wire immersed in 0.1 M AgCl and separated from the working electrode by a ceramic tip (Bioanalytical Systems Inc.) served as the reference electrode.

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