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Effect of Electrochemical Oxidation on Physicochemical Properties of Fe-Containing Single-Walled Carbon Nanotubes

Elli Leppänen [a], Sami Sainio [b,c], Hua Jiang [d], Bjørn Mikladal [e], Ilkka Varjos [e] and Tomi Laurila*[a]

Dedicated to the memory of Prof. Jingdong Zhang.

Abstract:
Metal catalysts are necessary for fabricating carbon nanotubes, but are often considered impurities in the end products, and arduous steps are used to remove catalyst residues from the nanotube structure. However, as metals can be electrocatalytic, instead of removing them, we can utilize their role in detection of analgesics. Here we study the physicochemical properties of Fe-containing single-walled carbon nanotubes (SWCNTs), and the effect of simple oxidative pretreatment on them. We show that a gentle anodic pretreatment (i) increased the amount of oxidized Fe nanoparticles, most likely exhibiting phases Fe₃O₄ and Fe₂O₃ and (ii) effectively removed disordered carbonaceous material from SWCNT bundles surfaces. Pretreatment had only a marginal effect on sensitivity towards paracetamol and morphine could be modified with pretreatment. Through this kind of in-depth investigation, we can to a certain extent, correlate various material properties of SWCNTs with the observed electrochemical performance. This approach allows us to evaluate what factors in SWCNTs truly affect the electrochemical detection of biomolecules.

Introduction
Carbon nanotubes (CNTs) have gained a great deal of attention in the past decades due to their unique properties, and they are widely investigated as electrode materials in electroanalytical applications for the detection of various biomolecules. The characteristics such as large surface area, high electrical conductivity and ability to catalyze redox reactions,[1–4] make CNTs an attractive material for electrochemical sensors. In fact, we have shown that as-fabricated pristine CNTs are a suitable material for the detection of neurotransmitter dopamine[5,6] and analgesics such as oxycodone[7], fentanyl[8], morphine and codeine[9]. The main methods for fabricating CNTs are chemical vapor deposition, electric discharge and laser ablation, where transition metal particles (Co, Fe, Ni) are used for catalyzing the growth of CNTs.[10] Due to the fabrication conditions, as-synthesized CNTs typically consist of residual metal particles, as well as a carbonaceous impurities, for example amorphous carbon and graphitic particles.[11,12] As the use of high-purity CNTs is generally emphasized in several applications, CNTs are often further processed. Purification of CNTs is a multistep and time-consuming process that generally requires the use of various concentrated acids and/or high temperatures, in order to remove the metal catalysts from encapsulated carbon shells.[10,13,14] Often these methods damage the carbon nanotube structure and alter its properties.

Here, we investigate the effects of metal catalyst nanoparticles in CNTs for electroanalytical applications, instead of removing them with heavy and destructive purification methods. It is well known that metals can catalyze various electrochemical reactions. We have previously shown that the metal catalysts in carbon nanomaterials have an essential role in the sensitivity and selectivity towards a different biomolecules, which cannot be achieved only with pure carbon[15,16]. Furthermore, we have extensively studied the suitability of pristine iron containing single-walled carbon nanotubes (SWCNTs) for the detection of various analgesics.[7–9] Despite these studies, at this stage, there are no clear indications regarding the required amount of iron that enhances electrocatalysis towards opioids, and whether the electrocatalytic properties of Fe-SWCNTs be improved with simple oxidative pretreatment.
Thus, in this work we study the role of Fe catalyst nanoparticles and their chemical composition, in the electroanalytical performance of single-walled carbon nanotube network. Fast and only marginally destructive anodic electrochemical pretreatment is performed, for clearing amorphous carbonaceous residual material from Fe particle surfaces as well as from surfaces of SWCNT bundles. The influence of electrochemical oxidation on the physicochemical properties of the SWCNTs is compared to the pristine SWCNTs. Aim of this study is to correlate the changes in these material properties to the observed electrochemical performance, to a certain extent. The structural changes are investigated in detail with high-resolution transmission electron microscopy (HRTEM). Changes in the surface chemistry and oxidation state of the Fe nanoparticles are studied by X-ray absorption spectroscopy (XAS). The electrochemical performance of the oxidized SWCNTs are investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) with outer-sphere probes Ru(NH$_3$)$_6$$_{2+3-}$ and Fe$_{2+3-}$ as well as inner-sphere systems including paracetamol (PA), morphine (MO) and oxycodone (OXC).

**Results and Discussion**

**HRTEM Analysis**

Figure 1 shows the TEM micrographs of pristine SWCNT networks in low and high magnification, as well as SWCNT networks that have been electrochemically oxidized at 1 V and 1.3 V. As seen from Figure 1A, the SWCNT network is very dense with high amount of single-walled carbon nanotubes and Fe nanoparticles. The HRTEM micrographs at high magnifications show clearly that the SWCNTs exist mainly in bundles. In case of pristine SWCNT networks (Fig. 1B), the metallic Fe particles are mostly covered with approximately 2 to 3 layers of a graphitic shell. Furthermore, it can be seen that the as-prepared SWCNT bundles are covered with an amorphous-like carbonaceous material, which is also observed with electrochemically pretreated 1 V
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Further structural investigation was carried out with a high-resolution scanning transmission electron microscope (STEM). The dark-field micrograph (Fig. 2A) illustrates the size distribution of Fe nanoparticles in a pristine SWCNT network. Interestingly, in addition to larger metallic Fe nanoparticles, smaller Fe particles are observed as incorporated in the carbon nanotubes themselves. These findings are also supported by the energy-dispersive spectrometer (EDS) elemental maps (Supporting Information).

In contrast, the pretreated samples with 1 V and 1.3 V anodic potentials mainly contain oxidized iron nanoparticles as illustrated in Figures 2B and 2C. These findings indicate that a mild and short electrochemical anodic pretreatment can already oxidize Fe nanoparticles. Most likely, the oxidation only takes place on particles that are either covered with disordered carbon or are totally exposed due to the fabrication process. In the dark-field micrographs, the oxidized iron has less well defined and blurry outline compared to the metallic Fe, which can be clearly observed from Figure 2. Both dark- and bright-field micrographs in Figure 3 clearly demonstrate the difference between the oxidized and metallic Fe nanoparticles, where the metallic iron phase is protected by graphitic layers. To confirm that the protected Fe particles indeed are mainly metallic Fe and unprotected are oxidized Fe, EDS analysis was performed at numerous locations (see Figures S2-S4). Small and bright particles observed on the SWCNT bundles in Figures 2B and 2C are gold (see Supporting Information and EDS analyses). Most likely, these Au particles are dissolved from the TEM grid during electrochemical oxidation in PBS, which has a high concentration of Cl- ions. The role of Au particles is not unambiguously known, but authors believe that Au does not have significant effect on electrochemical pretreatment process of SWCNTs.

From the high-resolution (S)TEM studies of the SWCNTs, the following conclusions can be made: (i) the pristine SWCNT network is covered to some extent with a disordered carbonaceous amorphous-like material that seems to be etched away (oxidized) at 1.3 V vs. Ag/AgCl. It indicates that at this potential, the SWCNT network can be cleaned from the excess amorphous carbon without destroying or inducing any significant effects onto the CNT structures. (ii) The pristine SWCNT contains mainly metallic Fe particles, whereas the 1 V and 1.3 V oxidized SWCNTs contain also oxidized Fe particles. Iron particles that are not affected by the electrochemical oxidation are encapsulated within graphitic layers that resemble well-ordered stable graphene sheets.

X-ray Absorption Spectroscopy

The surface chemistry and composition of iron particles, as well as CNT bundles, were further investigated with X-ray absorption
Figure 3. STEM A) dark- and B) bright-field micrographs from 1.3 V oxidized SWCNT network showing both metallic and oxidized Fe nanoparticle.

Figure 4. XAS A) C 1s, B) O 1s and C) Fe 2p spectra for pristine, 1 V and 1.3 V electrochemically oxidized SWCNT networks.

spectroscopy. Figure 4A displays the C 1s XAS spectra. All three SWCNTs show sharp and clearly defined long-ordered sp² bonding peak at 291.65 eV, as well as sp² π* peak at 285.2 eV, indicating high quality crystalline material [17–19] which is consistent with the XAS analysis of our previous work [20]. This clearly indicates that the electrochemical oxidation does not destroy the structure of the single-walled carbon nanotubes. The feature for carboxyl groups observed at energy 288.6 eV [21,22] for the oxidized samples with 1 V and 1.3 V, most probably arises largely from the glass substrate used. However, a clear difference is seen between the 1 V and 1.3 V SWCNTs, with the disappearance of the shoulder-like feature at 287.6 eV, demonstrating that with a higher anodic potential, the content of some specific surface group decreases. This could be due to the decrease in the C-H functionalization of the surface [23].

The Fe 2p XAS spectra for the SWCNT samples are shown in Figure 4B. In the L₃ - edge, the observed peak at lower energy arises from metallic Fe, whereas the higher peak comes from oxidized Fe [24]. For the pristine SWCNTs, both metallic and oxidized phases of Fe are seen. Intensity of the iron oxide peak enhances significantly when the SWCNTs are electrochemically pretreated. Based on the extensive literature survey [24–29], Fe 2p spectra of the 1 V and 1.3 V oxidized samples are similar to Fe₂O₃ with separate and well-defined peak at lower energy. However, based on the HRTEM and EDS analysis both samples also contain metallic Fe nanoparticles with graphitic shells after the pretreatment. Thus, we suggest that the Fe 2p spectra for the 1 V and 1.3 V oxidized samples arise from a combination of phases of metallic Fe, Fe₃O₄ and Fe₂O₃. Presumably, the pristine SWCNT network contains more Fe₃O₄ than Fe₂O₃, as the feature observed in the L₂-edge before 720 eV is proposed to arise from Fe²⁺ state [26,27]. With the 1.3 V oxidized sample, the intensity of this feature decreases, which could be attributed to the increase in Fe³⁺ states, making Fe₂O₃ the more dominant phase, consistent with the increase in the amount of oxygen in the solution phase. Additionally, it is very likely that some carbon is dissolved into the iron as well [28,31]. Even though the surface oxide(s) cannot be
Figure 5. Cyclic voltammograms of A) 1 mM Ru(NH$_3$)$_6^{2+/3+}$ in 1 M KCl and B) 1 mM Fe$_{2+/3+}$ in 0.2 M HClO$_4$ with scan rate $v$ = 200 mV/s. Average $\Delta E_p$ values and standard deviation (n = 3) as function of scan rate are shown for both C) Ru(NH$_3$)$_6^{2+/3+}$ and D) Fe$^{2+/3+}$ redox couples.

Table 1. Electrochemical characterization of SWCNT network electrodes. Average values of $\Delta E_p$ and peak current ratio are shown for Ru(NH$_3$)$_6^{2+/3+}$ and Fe$^{2+/3+}$ at $v$ = 200 mV/s. For all samples n = 3.

<table>
<thead>
<tr>
<th></th>
<th>Ru(NH$_3$)$_6^{2+/3+}$</th>
<th>Fe$^{2+/3+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\Delta E_p$ (mV)</td>
<td>$\Delta E_p$ (mV)</td>
</tr>
<tr>
<td>Pristine</td>
<td>77 ± 1</td>
<td>613 ± 15</td>
</tr>
<tr>
<td>1 V</td>
<td>73 ± 4</td>
<td>568 ± 21</td>
</tr>
<tr>
<td>1.3 V</td>
<td>80 ± 2</td>
<td>527 ± 11</td>
</tr>
</tbody>
</table>

unambiguously identified, we can predict the most feasible structure using simple thermodynamic arguments. If we assume that some of the iron remains non-oxidized, we can deduce, based on the assumption that local equilibria is established at the interfaces, the thermodynamically most feasible structure of these particles simply based on the corresponding Fe-O binary phase diagram. At low temperatures (< 570 °C), when one starts from metallic Fe (core of the particle) and continues to increase the oxygen content until gaseous oxygen (atmosphere) is reached, the only structure that fulfills the requirement of local equilibrium is α(Fe)/Fe$_3$O$_4$/Fe$_2$O$_3$. From the O 1s spectra in Figure 4C, one can observe a slight increase in the absorption intensity with increasing anodic pretreatment potential, which could be due to the increasing oxygen loading of the SWCNTs after the electrochemical pretreatment. With the 1.3 V sample, the O 1s spectrum has less clear shoulder-like feature around 530 eV and enhanced intensity at ≈532 eV. Thus, the 1.3 V sample most likely has a more specific surface functionalization than the pristine SWCNT. The high broad peak observed at higher energy (~540 eV) most probably arises from the used glass substrates. Without any specific and clear features in the O 1s spectra, it is difficult to address if the oxygen is bonded to carbon or/ and iron. However, from the Fe 2p spectra and the high-resolution (S)TEM analysis, it is obvious that (i) oxygen loading of the system increases after anodic pretreatment, and (ii) oxygen reacts with the iron nanoparticles.

Electrochemical characterization

The electrochemical properties of the SWCNTs were characterized with several redox probes. Possible effects of the anodic pretreatment on the electron transfer kinetics were studied with outer-sphere probe Ru(NH$_3$)$_6^{2+/3+}$, which is well-known to be insensitive to the surface chemistry of the material [32]. Figures 5A, 5C and Table 1 show that the electrochemical oxidation does not
have any significant effect on $\Delta E_{p,a}$ of the SWCNTs within the standard deviation. All the SWCNT networks exhibited quasi-reversible behavior with increasing $\Delta E_{p,a}$ as a function of scan rate.

Changes in the surface chemistry of the SWCNT networks were evaluated with Fe$^{2+/3+}$ redox couple. This probe is known to exhibit sluggish outer sphere redox kinetics in the absence of bridging ions. It has been suggested that in addition to Cl$^-$, also the sluggishly outer sphere redox kinetics in the absence of bridging electrode microstructure also plays an important role in the obvious that in addition to the surface chemistry, the carbon surface of SWCNT bundles. Based on these results, it is quite clear that in case of detection of PA, MO and OXC, there seems to be no significant difference in the active properties of the pristine SWCNTs are expected to be similar to that of the 1 V sample, as observed from background signals in PBS with a potential window of -0.4 - 1.0 V (see Figure S5). Results for all three analesics measured with the 1 V and 1.3 V oxidized SWCNT networks are shown in Figure 6. The average peak current $i_{p,a}$ and the oxidation potential $E_{p,a}$ values, with standard deviation, for the lowest and highest measured concentrations of PA, MO and OXC are collected in Table 2. For MO, values of the first oxidation peak around ~0.4 V are only shown, as it is most frequently used for determining morphine [9,36,37]. Interestingly, no remarkable changes in the sensitivity towards any of the biomolecules were observed, even though clear physical and chemical changes were observed with XAS and TEM/STEM. Thus, at least in case of detection of PA, MO and OXC, there seems to be no significant difference in the active electrochemical area, whether majority of the Fe nanoparticles are in metallic or in oxidized state in the SWCNT network. Interestingly however, the kinetics of the PA and MO are altered by the pretreatment, as seen from the shifts in the oxidation potentials, to cathodic and anodic directions, respectively. In case of PA, it is possible that the oxidized form of PA (the product) adsorbs more strongly on the surface of the 1.3 V sample, shifting $E_{p,a}$ towards more cathodic potentials, whereas the opposite phenomenon might take place with MO, where reduced form of MO (the reactant) adsorbs on the surface of the 1.3 V oxidized SWCNT. These observed behaviors with the 1.3 V oxidized SWCNT network could be due to (i) higher content of oxidized Fe particles, (ii) increase of clean surface of SWCNT bundles or (iii) altered oxygen loading at the carbon surface.

Effect of the chemical nature of the Fe particles on electrochemical detection of analgesics was studied with paracetamol, morphine and oxycodone. Only the results of the 1 V and 1.3 V pretreated SWCNTs are discussed here, as properties of the pristine SWCNTs are expected to be similar to that of the 1 V sample, as observed from background signals in PBS with a potential window of -0.4 - 1.0 V (see Figure S5).

### Table 2. Average values of background subtracted peak currents and oxidation potentials for lowest and highest measured concentrations of PA, MO and OXC ($n = 3$).

<table>
<thead>
<tr>
<th></th>
<th>1 µM PA</th>
<th>10 µM PA</th>
<th>1 µM MO</th>
<th>10 µM MO</th>
<th>1 µM OXC</th>
<th>10 µM OXC</th>
</tr>
</thead>
<tbody>
<tr>
<td>$i_{p,a}$ (nA)</td>
<td>43 ± 1</td>
<td>432 ± 6</td>
<td>28 ± 3</td>
<td>404 ± 4</td>
<td>192 ± 7</td>
<td>384 ± 4</td>
</tr>
<tr>
<td>$E_{p,a}$ (mV)</td>
<td>356 ± 14</td>
<td>384 ± 11</td>
<td>783 ± 8</td>
<td>783 ± 5</td>
<td>114 ± 28</td>
<td>792 ± 14</td>
</tr>
</tbody>
</table>

Figure 6. Electrochemical detection with DPV of A) paracetamol, B) morphine and C) oxycodone with 1 V and 1.3 V SWCNTs in PBS. For every analyte average $i_{p,a}$ values ($n = 3$) are shown as function of concentration, where $c_{PA} = 1, 10, 100, 1000 \mu M$ and $c_{MO} = c_{OXC} = 1, 2.5, 5, 10 \mu M$.
Although the exact origin of these changes in \( E_{\text{pa}} \) can’t be unambiguously specified, these results demonstrate the possibility of altering the selectivity properties of the SWCNT networks with simple electrochemical pretreatments.

**Conclusion**

Here we demonstrate the effect of electrochemical pretreatment on the physicochemical properties Fe-containing SWCNT networks. Both metallic and oxidized phases of iron were observed with the untreated pristine SWCNT network, whereas with mild anodic pretreatment the content of oxidized Fe nanoparticles increased. Some of the Fe particles that were protected by a few layers of graphene remained mainly metallic.

On the basis of the XAS results in this study and simple thermodynamic arguments, we suggest that both FeO and FeO\(_2\) phases are present with the oxidized SWCNTs. Interestingly, it was also shown that only the disordered carbonaceous amorphous-like material was etched away from the SWCNT bundles’ surface, without destroying the crystalline CNT structure or graphic shell around the metallic Fe particles.

Furthermore, we also showed that only a marginal effect was seen in the detection of analgesics, indicating that changes in the Fe nanoparticles phase do not play a key role in improving the SWCNTs sensitivity. However, the selectivity of SWCNTs can be tailored to some extent, as oxidation peak potentials were shifted in the case of both paracetamol and morphine, as a result of the electrochemical pretreatment. To understand more deeply the electrocatalytic properties of Fe-containing SWCNTs in electroanalytical applications, future works need to address also the other SWCNT properties, such as the size of CNT bundles or iron loading in the structure.

**Experimental Section**

**Sample fabrication**

The SWCNT networks were fabricated by a high-temperature floating catalyst chemical vapor deposition in laminar flow reactor. Briefly, in this process an iron precursor is introduced into a carbon monoxide atmosphere, where it thermally decomposes to iron nanoparticles. Subsequently, these iron particles catalyze the growth of SWCNTs by decomposing carbon monoxide. SWCNTs formed in the gas phase were collected using a membrane filter. The fabrication process is described in more detail in [38,39].

The fabricated SWCNT networks were press-transferred onto a glass substrate (Thermo Scientific, ISO 8037/I). First 10 x 26 mm pieces were cleaved from microscope slides and cleaned with K\( \text{MnO}_2 \) procedure, where the glass substrates were first soaked in K\( \text{MnO}_2 \) overnight. After soaking, the substrates were rinsed with diluted H\( \text{O}_2 \)+H\( \text{2SO}_4 \) solution, boiled in deionized water three times and dried at room temperature. Then smaller SWCNT pieces were cut from the A4 sheet and press-transferred by placing SWCNT network side to the glass substrate. After peeling off the filter support, SWCNT network was densified by drop-casting 4 ml of 99.5 p-% ethanol on top of the network. Electrical contact of the electrode was prepared by painting a silver pad with conductive silver paint (Electrolube). Then the sample was covered with inert PTFE-tape (Sain-Gobain Performance Plastics CHR 2255-2) with a 3 mm hole, which was placed on top of the SWCNT network to define the working area of the electrode.

Three types of SWCNT electrodes are used in this study: pristine (as-prepared) and two electrochemically pretreated (oxidized) electrodes. The electrochemical pretreatment is carried out in 10 mM phosphate buffered saline (PBS, pH 7.4) by holding the electrode either at 1 V or 1.3 V (vs. Ag/AgCl) for 5 minutes. Chronoamperograms of the pretreatment process and cyclic voltammograms recorded afterwards are shown in Supporting Information (see Figures S6 – S8).

**HRTEM**

All three samples were characterized with both high-resolution TEM and STEM using a JEOL JEM-2200FS double aberration-corrected microscope equipped with X-ray EDS detector [40]. The microscope was operated at 200 kV. The high resolution images were recorded with a Gatan 4k x 4k UltraScan 4000 CCD camera. The pristine SWCNT sample was press-transferred directly on a gold-copper TEM grid (Agar Scientific). For the 1 V and 1.3 V samples, electrodes were prepared in similar manner as described above with the exception that the TEM grid was first applied on a glass substrate and SWCNT network was placed on top of the grid. These electrodes with the TEM grid were then subject to the oxidative pretreatment. After the electrochemical pretreatment, samples were washed with deionized water and dried in room temperature. Then the grids with the pretreated SWCNTs were removed from the glass substrates and used in (S)TEM measurements.

**XAS**

The soft X-ray XAS measurements were carried out at the Stanford Synchrotron Radiation Lightsource (SSRL), on a bending magnet beamline 8-2 using a 55° incidence angle (magic angle) of X-rays. Beamline 8-2 is equipped with a spherical grating monochromator, which is operated using 40 x 40 μm slits resulting in a resolution of around 200 meV. Beam spot size at the interaction point was around 1 x 1 mm\(^2\) with total flux in the order of 10\(^{10}\) photons / sec. The X-ray energy for the carbon and oxygen 1s edge were from 260 eV to 340 eV and 520 eV to 560 eV, respectively. Both the data were collected in total electron yield (TEY) mode using the drain current amplified by a Keithley picoammeter. The incoming flux was recorded using a nickel grid with Au sputtered film. A reference sample was used to cut about 10 % of the beam during the measurements, which was used for energy calibration of the data prior to the data analysis. All the data were background subtracted and energy corrected using IGOR Pro v. 8.06 software.

The electrochemically pretreated SWCNTs at 1 V and 1.3 V were prepared as described previously on a glass substrate, whereas the pristine SWCNT was press-transferred on a highly conductive boron doped Si <100> wafer (Siegler Wafer). All three samples were attached to an aluminum stick with adhesive carbon tape. After the initial reference sample energy alignment, the C 1s spectra were confirmed to match their energy calibration by observing the core-exciton signature present at 291.65 eV [17–19]. Similarly, the Fe 2p spectra were further energy aligned to metallic iron feature at 707.36 eV according to Regan et al. [20]. The O 1s spectra were not energy aligned as no clear fingerprints were observed. The pristine SWCNT Fe 2p spectrum was normalized to match the intensity of metallic iron in the 1 V sample. Otherwise
all data presented in Figure 5 show the absolute intensity of C 1s, O 1s and Fe 2p.

**Electrochemical measurements**

Cyclic voltammetry (CV) was carried out with a Gamry Reference 600+ potentiostat, whereas differential pulse voltammetry (DPV) was conducted with a CH Instruments (CHI630E) potentiostat. A three-electrode cell was used in all measurements with an Ag/AgCl reference electrode (+0.199 V vs. SHE, Radiometer Analytical) and a Pt wire (Goodfellow) counter electrode. The CV measurements were done in 1 mM Ru(NH₃)₆²⁺/³⁺ and 1 mM Fe²⁺/³⁺, where hexaammineruthenium(III) chloride (Sigma-Aldrich) was dissolved in 1 M KCl (Merck Suprapur, pH 6.8) and ammonium iron(II) sulfate hexahydrate (Sigma-Aldrich) in 0.2 M HClO₄ (VWR Chemicals, pH 1). Inert supporting electrolyte was used with Fe²⁺/³⁺ to avoid possible catalyzing effect of free Cl⁻ ions [41]. The Electrochemical measurements. This project was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under contract number DE-AC02-76SF00515.

Keywords: Electrochemistry • Electron microscopy • Iron nanoparticles • Single-walled carbon nanotubes • X-ray absorption spectroscopy

**References**


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With short electrochemical pretreatment, exposed Fe catalyst nanoparticles in single-walled carbon nanotube (SWCNT) networks oxidize from metallic Fe to phases of Fe$_3$O$_4$ or Fe$_2$O$_3$, whereas encapsulated Fe nanoparticles remain metallic. It is shown that the pretreatment can be used to modify SWCNT network selectivity towards analgesics, whereas interestingly no remarkable changes are seen in the sensitivity.