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Strong p-Type Doping of Individual Carbon Nanotubes by Prussian Blue Functionalization**

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Numerous efforts have been devoted to the application of single-walled carbon nanotubes (SWCNTs) in nanoscale electrical devices, including field-effect transistors (FETs),^[1,2] memories,^[3] and (bio)chemical sensors.^[4] These activities have strongly benefited from the development of methods enabling the controlled chemical functionalization of CNTs.^[5] Among these techniques, noncovalent modification schemes have found application in the chemical doping of nanotubes,^[6] for example for the conversion of semiconducting SWCNTs from p- to n-type,^[7] and the fabrication of p-n junctions within individual SWCNTs.^[8] Such doping has mainly been realized using alkali metals and amino-polymers (e.g., polyethyleneimine^[9]) for n-type, and halogens^[10] or FeCl₃^[11] for p-type doping. A class of potential dopants that has received comparatively little attention so far is that of metal coordination compounds. One such compound, Prussian Blue (PB) (Fe^{III}₄[Fe^{II}(CN)₆]₃ · nH₂O (n = 14–16)), has been utilized as an electrocatalytic material to modify bulk CNT electrodes with the aim of fabricating amperometric biosensors.^[12] However, while these studies have addressed the electrochemical properties of the resulting modified electrodes in detail, the impact of the PB layer on the electronic properties of the underlying nanotubes remained unexplored. Furthermore, decorating CNTs with PB is of interest because of the fact that PB is a molecular magnet displaying ferromagnetic properties below its Curie temperature of $T_c = 5.6$ K,^[13] which potentially opens up the possibility for their application in spintronic devices. In the present work, we focus on the electrical properties of individual SWCNT

modified with an ultrathin layer of PB. To functionalize individual SWCNTs with PB, we employ electrodeposition from aqueous solutions containing ferric (Fe³⁺) and ferricyanide ([Fe^{III}(CN)₆]³⁻) ions, similar to studies on bulk samples.^[14] In contrast to electroless deposition,^[15] electrodeposition offers the advantage of control over the deposited amount, and furthermore favors selective coating of the electrified surface.^[16] Most notably, PB-modified semiconducting SWCNTs were found to exhibit a temperature-dependent doping characteristic, ranging from heavy p-type doping at room temperature to negligible additional doping at cryogenic temperatures.

In order to prove the presence of PB on the SWCNTs modified by electrodeposition, low-density nanotube networks were investigated using different spectroscopic techniques. An AFM image of such a network coated by PB is presented in Figure 1, which reveals dense particle coverage on the tubes. Detailed AFM analysis has shown that the size of these particles ranges between 10 and 100 nm.

The UV-visible absorption spectrum of the PB-coated networks exhibits a broad absorption band with a maximum at about 700 nm (Figure 2a). This feature can be assigned to photoinduced charge transfer between Fe(II) and Fe(III) centers in the PB.^[17] X-ray photoelectron spectroscopy (XPS) data collected from a PB-covered SWCNT network are depicted in Figure 2b,c. Of strongest relevance are the iron and nitrogen peaks, whose energies determined from curve fits are presented in Table 1 along with literature values for comparison. The N(1s) peak occurring at 397.7 eV indicates the presence of nitrogen in the cyano ligand, while the shoulder at 399.3 eV and the weak peak at 402.3 eV most likely originate from surface contaminations. A detailed analysis of the iron peaks is complicated by the fact that the binding energy of the Fe ions is affected by multiplet splitting, satellite features and different oxidation states.^[18] This has led to considerable discrepancies in the peak assignments as reported in the literature. The Fe 2p area is composed of two groups of peaks, each of which could be fitted by three components (Figure 2c). Comparison with the literature values indicates that the group at lower binding energy with components at 708.4 eV, 709.7 eV, and 712.9 eV comprises the Fe 2p_{3/2} signal, while the higher energy group with components at 721.2 eV, 722.8 eV, and 725.3 eV corresponds to Fe 2p_{1/2}. Moreover, the peaks at 708.4 eV and 721.2 eV can be reasonably assigned to Fe(II), and the peaks at 709.7 eV and 722.8 eV to Fe(III). On this basis, the two remaining peaks at 712.9 eV and 725.3 eV could be explained as satellites belonging to Fe(II) that occur because of surface reduction of high-spin Fe (III) to high-spin Fe (II), in accordance with previous observations.^[18,19]

In order to discriminate between the effect that PB functionalization has on the electric transport properties of metallic and semiconducting SWCNTs, it is crucial to investigate PB coated individual SWCNTs. When the same electrodeposition conditions utilized to coat the SWCNTs networks were applied to individual metallic or semiconducting SWCNTs bridging two metal electrodes with a separation of ~100 nm, a dense coating was formed on both types of tubes due to sizeable electrodeposition occurring in the vicinity of

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Supporting Information is available on the WWW under <http://www.small-journal.com> or from the author

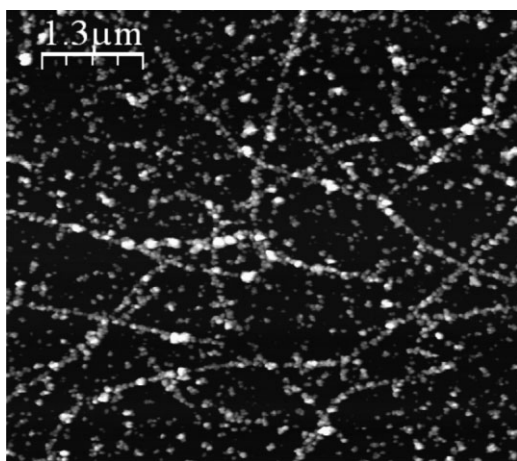


Figure 1. AFM image of a typical SWCNT network on a Si/SiO₂ substrate after electrochemical deposition of Prussian Blue. The electrode used to contact the network is located out of the scan range.

the electrode edges. In case of metallic SWCNTs, the PB coating did not alter the electrical resistance (Figure S1, Supporting Information). This observation proves that neither covalent bonding between the CNT and the PB takes place, nor are defects introduced by the electrochemical modification, similar to previous studies on the noncovalent modification of metallic tubes.^[5] In fact, covalent attachment is documented to disturb the sp² carbon network by introducing sp³ conjugated carbons, thereby significantly reducing the tube's conductivity.^[20] Moreover, the presence of sp³ centers or other types of defects would be manifested in a noticeable gate dependence of conductance,^[20] which is, however, not observed (Figure S1, Supporting Information).

Contrary to the metallic case, the electrical transport properties of semiconducting SWCNTs were found to be strongly influenced by electrochemical functionalization with PB. It can be discerned from Figure 3 that the pristine semiconducting tubes display the characteristic p-type behavior (black curve), i.e., decreasing current with increasing gate voltage.^[1,21] The observed high ON conductance approaching 0.4 G_0 (with $G_0 = 2e^2/h$ being the conductance quantum^[22]) indicates the absence of sizeable Schottky barriers at the contacts. A strikingly different behavior, namely the complete absence of gate dependence under ambient conditions (red curve), is found after PB coating.^[23] The study of SWCNTs with a different density of PB deposited on top revealed that such altered gate dependence requires almost full coverage by a PB layer (see Supporting Information). The vanishing of gate dependence can be explained by strong p-doping of the nanotube whereupon the threshold voltage is shifted toward much higher gate voltage (out of the experimentally accessible range). Such type of doping is consistent with the electron transfer from the nanotube to Fe(III) ions in the PB deposition solution that occurs during the electrodeposition process. As the electrodeposition solution is acidic (pH = 2), control experiments were performed wherein PB was deposited in an electroless manner^[15] onto semiconducting SWCNTs, using a bath of the same pH. The obtained results clearly demonstrate that the PB coating is responsible for the observed effect,

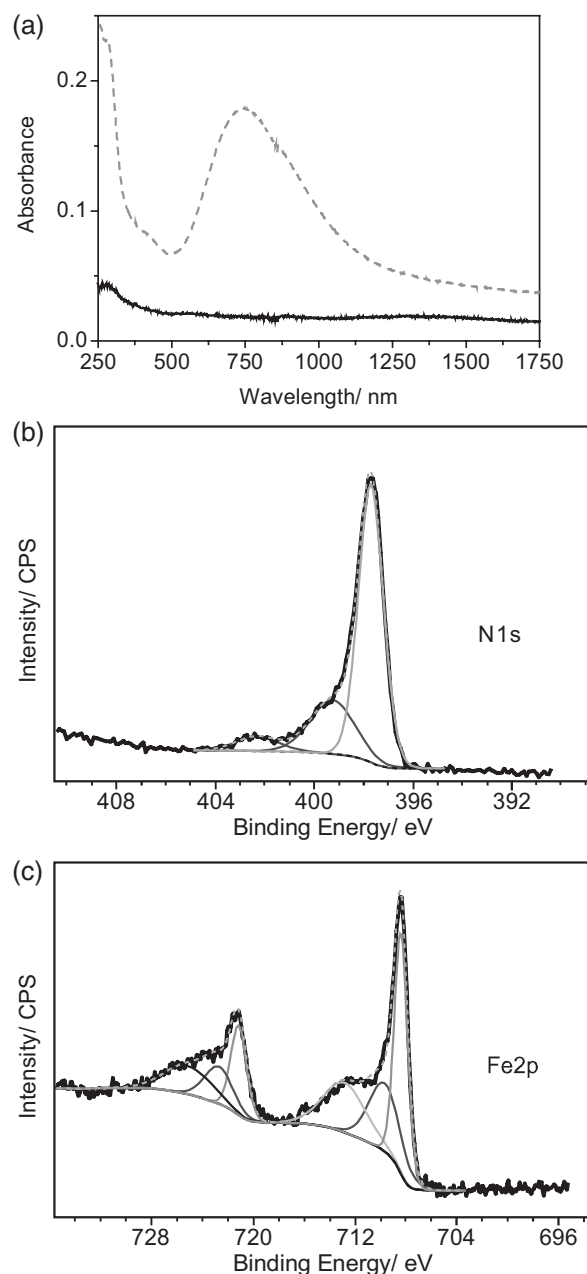


Figure 2. a) UV/Vis absorption spectra of a SWCNT network before (solid line) and after (dashed line) electroless deposition of PB. b, c) X-ray photoelectron spectra of a SWCNT network modified by PB electrodeposition, corresponding to the N 1s (b) and Fe 2p (c) regions.

although an additional doping contribution by H₃O⁺ ions under the applied potential^[20,24] cannot be ruled out. The possibility that a layer of PB deposited between the metal electrodes contributes to the electrical conduction could be excluded by test experiments wherein electrode gaps were closed by electrodeposited PB, which yielded very high resistances exceeding 10 GΩ (Figure S2, Supporting Information).

Temperature-dependent electrical studies of the PB-decorated semiconducting nanotubes revealed a pronounced change in the electrical behavior upon cooling of the samples

Table 1. Survey of XPS Fe 2p and N 1s binding energies in PB (electrodeposited or commercial samples) reported in the literature and measured in the present work. The literature data include values of partially reduced PB, which may be formed by light-induced reaction at the surface.

	Binding energy [eV] (electrodepos. PB)	Binding energy [eV] (commercial PB)	Literature value [eV]	Assignment of peak in literature
	708.4 ± 1.2	708.1 ± 1.3	708.7–709.0	Fe (II) low spin unambiguously identified in lit.
Fe (2p _{3/2})	709.7 ± 2.8	709.7 ± 2.1	710–712 ^[19,33,34] (in some works not visible)	Fe (III)
	712.9 ± 3.9	713.1 ± 4.8	712.7 ^[35] (in some works not visible)	Fe(III) ^[35]
			713.6–713.8 ^[19,33] (in some works not visible)	Fe(II) high spin satellite ^[19]
Fe (2p _{1/2})	721.2 ± 1.4	721.1 ± 1.8	721–721.9 ^[33–35]	Fe (II)
	722.8 ± 2.6	723.0 ± 2.1	723.9 ^[34]	Fe (III)
	725.3 ± 4.1	725.7 ± 5.2	726.1 ^[35]	Fe(III)
N (1s)	397.7 ± 1.2	397.4 ± 1.1	397.8–398.2	N in CN unambiguously identified in lit.
	399.3 ± 2.1 ^[b]	398.8 ± 1.9	398.3	KCN ^[36] [a]
		400.1 ± 1.4	399.6–400.2 ^[34,35]	CN–surface ^[34]
	402.3 ± 2	401.8 ± 2		Charge transfer ^[35]

[a]Potassium peaks corresponding to KCN have also been detected in commercial PB powder, but not in our electrodeposited PB.

[b]This peak is also observed on Si/SiO₂ substrates with electrodes but without CNTs and without PB.

(Figure 3). In particular, upon lowering the temperature to 50 K (blue curve), full recovery of the original gate dependence, comprising a current modulation over more than five orders of magnitude, is observed. The samples could be reproducibly cycled between p-type behavior and negligible gate dependence by repeated heating and cooling. The decrease in current with decreasing temperature (at fixed positive gate voltage) could originate from a temperature dependence of the charge carrier mobility or the charge carrier density in the tubes. In view of the almost identical ON currents detected at the various temperatures, the existence of a significant temperature dependence of mobility can be

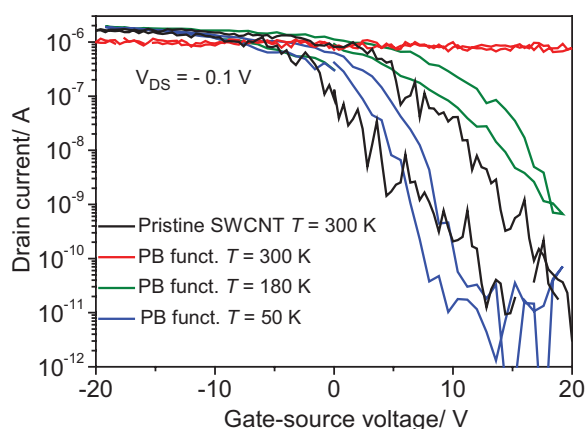


Figure 3. Drain current as a function of applied gate-source voltage for an individual semiconducting SWCNT. The black curve shows the gate dependence of the pristine tube at room temperature, while the red, green and blue curves belong to the same nanotube after electrodeposition of PB, measured at the three indicated temperatures.

excluded. Accordingly, the most plausible scenario is that upon lowering the temperature, the transfer of holes from the PB to the nanotube is frozen out. This explanation is consistent with the theoretical prediction of a threshold shift toward negative (or positive) gate voltages with increasing n- (or p-) type level.^[25]

The modified nanotubes were further characterized by Raman spectroscopy. As exemplified by Figure 4, the Raman spectrum of PB-coated semiconducting SWCNTs displays a prominent peak at approximately 2164 cm⁻¹ attributable to the C–N stretch vibration in the PB.^[26] In addition, the D- and G-band of the underlying nanotube appear near 1325 cm⁻¹

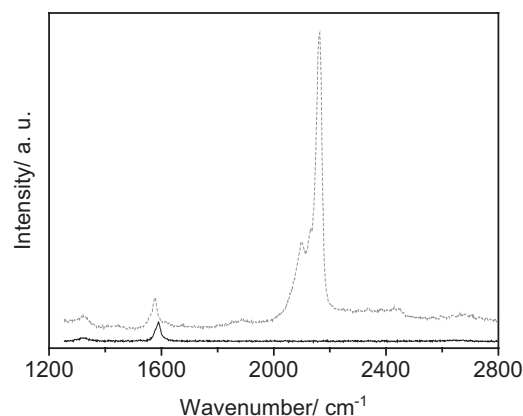


Figure 4. Raman spectra ($\lambda_{\text{exc}} = 633 \text{ nm}$) acquired with a confocal microscope from an individual semiconducting SWCNT before (solid line) and after (dashed line) PB electrodeposition.

and below 1600 cm^{-1} , respectively. The only slight increase of the D-band intensity compared to the pristine tube testifies that the PB predominantly attaches in a noncovalent manner, in close correspondence to the results of the electrical measurements. Interestingly, the G-band maximum is found to be downshifted in energy (by 12 cm^{-1}) because of the PB coating. At first sight, this shift direction is unexpected since p-type doping should lead to an upshift of the G-band according to observations made upon chemical^[27] or electrochemical^[28] oxidation of SWCNTs. One tentative explanation for the downshift involves extensive local heating of the nanotube, which may be enhanced by the strong optical absorption of the PB coating. Heating-induced downshifts of the radial breathing mode (RBM) and the G-band are well-documented for SWCNT bulk samples.^[29] However, the minimum temperature needed to account for the present downshift of the highest intensity G-mode by $\sim 10\text{ cm}^{-1}$ would be quite high (using a temperature coefficient of $-0.025\text{ cm}^{-1}\text{ }^{\circ}\text{C}^{-1}$,^[29] a value of $\sim 400\text{ }^{\circ}\text{C}$ is estimated). More detailed investigations are hence needed in order to further clarify the Raman properties of the PB-modified nanotubes.

In summary, it was found that the functionalization of individual SWCNTs by electrodeposition of Prussian Blue (PB) leaves metallic tubes unaffected, whereas semiconducting tubes are strongly p-doped. The temperature-dependent electrical properties of PB-functionalized semiconducting tubes can be understood by the freeze-out of the transfer of holes from the PB to the nanotube below 100 K. Carbon nanotubes decorated by PB represent a valuable model system for nanowires coupled to ferromagnetic spin chains, which are expected to show interesting electrical transport features under an applied magnetic field.^[30]

Experimental Section

Single-walled carbon nanotubes were synthesized by iron particle-catalyzed chemical vapor deposition (CVD) on highly doped Si/SiO₂ substrates (200 nm oxide thickness), as previously described.^[31] Individual nanotubes were located with the aid of an atomic force microscope (Nanoscope IIIa, Digital Instruments; image analysis with WSxM software^[32]) in tapping mode, and provided with 0.3 nm/15 nm Ti/AuPd contacts (100 nm separation) defined by standard electron-beam lithography. Electrodeposition of PB was performed with a Solartron 1285 potentiostat (working electrode: contacted tube, counter electrode: Pt wire, reference electrode: Ag/AgCl) using a freshly prepared aqueous solution of FeCl₃ (0.2 mM) and K₃Fe(CN)₆ (0.2 mM) in HCl (5 mM). After application of a constant current density of approximately 3 nA cm^{-2} for 20 s, the samples were removed from the cell, rinsed and dipped in 10 mM HCl, thoroughly rinsed with water, and finally dried under nitrogen flow. Electroless PB deposition was accomplished through dipping the substrates for 15 min into a freshly prepared bath containing FeCl₃ (20 mM) and K₃Fe(CN)₆ (20 mM) in HCl (5 mM).

The optical absorption and XPS studies on SWCNT networks were performed using a Perkin-Elmer Lambda 19 UV-visible spectrometer and an AXIS ULTRA electron spectrometer, respec-

tively. Raman studies were carried out using a confocal microscope NTEGRA SPECTRA (NT-MDT) spectrometer (633 nm wavelength up to 9 mW). The low temperature electrical measurements were performed in an Oxford helium cryostat.

For further experimental details, see Supporting Information.

Keywords:

carbon nanotubes · doping · electrodeposition · Prussian blue

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