Supporting Information

Charge Transport in and Electroluminescence from sp³-Functionalized Carbon Nanotube Networks

Nicolas F. Zorn, Felix J. Berger, and Jana Zaumseil*

Institute for Physical Chemistry and Centre for Advanced Materials, Universität Heidelberg, D-69120 Heidelberg, Germany

Corresponding Author

*E-mail: zaumseil@uni-heidelberg.de
Raman and Absorption Spectroscopy of (6,5) SWCNTs ....................................................... S-3
Raman and Absorption Spectroscopy of sp³-Functionalized (6,5) SWCNTs ......................... S-4
Atomic Force Microscopy ..................................................................................................... S-5
Electrical Characterization of SWCNT FETs ..................................................................... S-6
  Transfer Characteristics and Voltage-Dependent Linear Mobilities ............................... S-6
  Output Characteristics ....................................................................................................... S-7
  Linear Mobilities _versus_ Defect Metrics ................................................................ S-8
  Frequency-Dependent Capacitance Measurements ....................................................... S-9
Spectroscopic Characterization of SWCNT FETs ............................................................. S-10
  Electroluminescence Spectroscopy ................................................................................ S-10
  Voltage- and Excitation Power-Dependent Photoluminescence Spectroscopy ............ S-13
  Estimation of Excitation Densities in EL and PL Spectroscopy of SWCNT Networks ... S-18
  Charge Modulation Photoluminescence Spectroscopy ................................................. S-20
Temperature-Dependent Electrical Characterization of SWCNT FETs ......................... S-23
  Extraction of Trap Densities from the Subthreshold Regime ........................................ S-23
  Schematic Device Layout and Principle of Gated Four-Point Probe Measurements ...... S-24
  Temperature-Dependent Mobilities ............................................................................. S-25
REFERENCES ................................................................................................................... S-26
Raman and Absorption Spectroscopy of (6,5) SWCNTs

Figure S1. Characterization of PFO-BPy-wrapped (6,5) SWCNTs. a) Raman spectrum of a drop-cast film of (6,5) SWCNTs in the radial breathing mode (RBM) region. The absence of other peaks confirms the high purity of the dispersion without residual metallic nanotubes or other minority species. The excitation wavelength was 532 nm, and the data was baseline-corrected and averaged over 4000 spectra. b) UV-vis-nIR absorption spectrum of a (6,5) SWCNT dispersion in toluene. The main excitonic transitions (E_{11}, E_{22}, E_{33}), the E_{11} phonon side band (PSB), and the absorption band of the wrapping polymer are indicated. No other absorption peaks corresponding to larger-diameter chiralities are observed in the nIR region up to 1600 nm.
Raman and Absorption Spectroscopy of sp³-Functionalized (6,5) SWCNTs

Figure S2. a) Raman spectra of drop-cast SWCNT films in the G-mode region and b) zoom-in on the D-mode. The increase in the D/G⁺ area ratio is attributed to a higher density of introduced sp³ defects for higher diazonium salt concentrations (c\textsubscript{DzBr}). For all spectra, the excitation wavelength was 532 nm, and the data was baseline-corrected and averaged over 4000 spectra.

Figure S3. a) UV-vis-nIR absorption spectra of pristine and sp³-functionalized SWCNT dispersions. b) Zoom-in on the E\textsubscript{11}⁺ defect state absorption band that increases with the diazonium salt concentration (c\textsubscript{DzBr}).
Atomic Force Microscopy

Figure S4. Atomic force micrograph of a dense, pristine SWCNT network used for the FET fabrication in this study. Scalebar is 1 µm.
Electrical Characterization of SWCNT FETs

Transfer Characteristics and Voltage-Dependent Linear Mobilities

**Figure S5.**

- **a)** Representative transfer characteristics (source-drain voltage $V_{ds} = -100$ mV) of ambipolar FETs based on dense networks of sp$^3$-functionalized (6,5) SWCNTs with different defect densities (drain currents $I_d$, solid lines; gate leakage currents $I_g$, dashed lines).
- **b)** Voltage-dependent linear charge carrier mobilities of pristine and sp$^3$-functionalized SWCNT network FETs. Only forward sweeps are shown for clarity.
Output Characteristics

**Figure S6.** Representative output characteristics of ambipolar FETs based on dense networks of a, b) pristine SWCNTs and c, d) sp³-functionalized SWCNTs with a high defect density in hole and electron accumulation, respectively.
Linear Mobilities versus Defect Metrics

Figure S7. a) Absolute linear charge carrier mobilities (holes, blue squares; electrons, red circles) of pristine and sp$^3$-functionalized (6,5) SWCNT network FETs vs. the Raman D/G$^+$ area ratio, the E$_{11}^*/$E$_{11}$ absorption area ratio, and the E$_{11}^*/$E$_{11}$ PL area ratio, respectively. b) Linear charge carrier mobilities normalized to the pristine reference vs. defect metrics. Displayed values are maximum carrier mobilities and were averaged over several devices, error bars are standard deviations.
Frequency-Dependent Capacitance Measurements

**Figure S8.** Normalized frequency-dependent capacitance of pristine and sp³-functionalized SWCNT network FETs measured in the on-state of the devices (gate voltage \( V_g = -5 \) V). The decrease in charge carrier mobilities results in a lower cut-off frequency of the transistors.

**Table S1.** Areal capacitances of pristine and sp³-functionalized SWCNT network FETs extracted in the on-state of the devices.

| Sample                  | SWCNT network capacitance (nF/cm²) |
|-------------------------|-------------------------------------|
| Pristine                | 110                                 |
| Low defect density      | 118                                 |
| Medium-low defect density | 118                     |
| Medium-high defect density | 118                         |
| High defect density     | 117                                 |
Spectroscopic Characterization of SWCNT FETs

Electroluminescence Spectroscopy

Figure S9. EL spectra of a) pristine and b-e) sp³-functionalized SWCNT network FETs with different defect densities for different drain currents (corresponding gate voltages vary from -2.2 V to -5.0 V). With increasing level of sp³ functionalization, emission from the defect states becomes more dominant.
Figure S10. EL spectra normalized to the E_{11} exciton peak of a) pristine and b-e) sp³-functionalized SWCNT network FETs with different defect densities for different drain currents (corresponding gate voltages vary from -2.2 V to -5.0 V). sp³ Defect emission is stable over one to two orders of magnitude in current density. Only a slight decrease of the defect-to-E_{11} emission ratio with increasing drain currents is observed.
Figure S11. a) Log-log plot of the integrated EL intensity of a high defect density sp³-functionalized SWCNT network FET (corresponding spectra shown in Figure 3e of the main text) depending on the drain current. The slopes are ~1, indicating that the experiments were conducted in the linear excitation regime where no state-filling is expected. b) Comparison between a normalized PL spectrum (low-power, non-resonant continuous wave excitation at 785 nm) and a normalized EL spectrum.
Voltage- and Excitation Power-Dependent Photoluminescence Spectroscopy

Figure S12. **a**) Static, gate voltage-dependent PL spectra (source-drain voltage $V_{ds} = -10$ mV) of an sp$^3$-functionalized SWCNT network FET with high defect density in electron accumulation. **b**) Spectra normalized to the $E_{11}$ exciton peak. At high voltages, PL from negatively charged trions can be observed at very similar wavelengths to the $E_{11}^*$ emission. All spectra were acquired under non-resonant continuous wave excitation (785 nm, ~320 W cm$^{-2}$). Note that the peak at ~985 nm marked with an asterisk corresponds to the Raman 2D mode of (6,5) SWCNTs.
Figure S13. a, b) Static, gate voltage-dependent PL spectra (source-drain voltage $V_{ds} = -10$ mV) of a pristine (6,5) SWCNT network FET in hole and electron accumulation, respectively. c, d) Spectra normalized to the E$_{11}$ exciton peak. At high voltages, PL from positively and negatively charged trions, respectively, can be observed. All spectra were acquired under pulsed excitation at the E$_{22}$ transition (575 nm, $\sim$0.02 mJ cm$^{-2}$).
Figure S14. **a, b)** Static, gate voltage-dependent PL spectra (source-drain voltage \( V_{ds} = -10 \text{ mV} \)) of an sp\(^3\)-functionalized SWCNT network FET with high defect density in hole and electron accumulation, respectively. **c, d)** Spectra normalized to the E\(_{11}\) exciton peak. At high voltages, PL from positively and negatively charged trions, respectively, can be observed at very similar wavelengths to the E\(_{11}^*\) emission. All spectra were acquired under pulsed excitation at the E\(_{22}\) transition (575 nm, \(~0.02\text{ mJ cm}^{-2}\)).
Figure S15. Excitation power-dependent PL spectra of an sp\(^3\)-functionalized SWCNT network FET with high defect density a) without applied bias (\(V_g = 0\) V) and b) at \(V_g = -2\) V under continuous wave excitation (785 nm). c, d) Spectra normalized to the E\(_{11}\) exciton peak show saturation of E\(_{11}^*\) and E\(_{11}^{*}\) emission at higher excitation densities. Note that the sharp peak at \(\sim985\) nm marked with an asterisk corresponds to the Raman 2D mode of (6,5) SWCNTs.
Figure S16. Excitation power-dependent, integrated PL intensities of an sp³-functionalized SWCNT network FET with high defect density a) without applied bias ($V_g = 0$ V) and b) at $V_g = -2$ V under continuous wave excitation (785 nm). Intensities were obtained from Lorentzian fits to the spectra in Figure S15. c, d) Ratios of the integrated PL intensities ($E_{11}^*/E_{11}$ and $E_{11}^{*-}/E_{11}$) show that the emission of $E_{11}^*$ and $E_{11}^{*-}$ defect states saturates at higher excitation densities when a voltage ($V_g = -2$ V) is applied (d) compared to the neutral state (c).
Estimation of Excitation Densities in EL and PL Spectroscopy of SWCNT Networks

To rationalize the differences in defect emission intensities relative to the $E_{11}$ exciton, we estimate the excitation densities in the different experiments as outlined in the following.

In EL measurements, the excitation density is determined by the source-drain current within the transistor channel. A current of 100 µA corresponds to $\sim 6.2 \times 10^{14}$ charges per second, which is identical to the number of excitons per second assuming that every charge carrier recombines to form an exciton. The total channel width is 10 mm (interdigitated electrodes) and we assume a width of 2 µm for the recombination zone. To calculate the areal density of SWCNTs, we use an average length of $\sim 1.5 \mu m$ and a linear density of $\sim 20 \mu m^{-1}$ for the dense networks. Thus, the areal density is $\sim 21$ SWCNTs per $\mu m^2$ using the formula from Statz et al. With an exciton lifetime of $\sim 100$ ps, we obtain an instantaneous excitation density of $\sim 1.5 \times 10^{-1}$ excitons per SWCNT. This calculation is identical to Naber et al. except that the quantum yield is not considered here, since we are interested in the overall excitation density rather than the exciton density available for lasing.

In PL experiments with pulsed laser excitation, samples were excited with the output of a supercontinuum laser (20 MHz repetition rate, $\sim 6$ ps pulse width, 575 nm excitation wavelength). The average laser power in the excitation spot was $\sim 10$ µW, corresponding to $\sim 1.5 \times 10^6$ photons per pulse. With the photon energy, we can calculate the number of photons per time and per pulse. To estimate the number of absorbed photons, the peak absorption coefficient for excitation at the $E_{22}$ transition as determined by Streit et al. and the geometrical factor of 88,000 carbon atoms per $\mu m$ nanotube length for (6,5) SWCNTs are used. With an areal density of $\sim 21$ SWCNTs per $\mu m^2$ as detailed above, and a laser spot size of $\sim 2 \mu m$ in diameter, we calculate an excitation density of $\sim 3.4 \times 10^1$ excitons per SWCNT and pulse. This result is in good agreement with Ma et al. who estimated $\sim 3$ $E_{11}$ excitons per 1 µW pump laser power for pulsed excitation at the $E_{22}$ transition.

Consequently, the exciton densities under pulsed optical excitation are significantly ($\sim 100$ times) higher compared to electrical excitation. Due to state filling, $sp^3$ defect emission saturates at lower excitation powers than emission from the mobile $E_{11}$ exciton. Hence, the difference in defect emission intensities (considerably higher defect emission in EL compared to PL under pulsed $E_{22}$ excitation) is inferred to result from the different excitation density regimes.
For PL experiments under continuous wave excitation at 785 nm, the density of generated excitons cannot be estimated since the absorption cross section for this off-resonant excitation wavelength is unknown. However, from the laser power-dependent PL measurements (see Figures S15 and S16), it is evident that excitation powers for the acquisition of the spectra in Figures 4 and S12 were in the linear regime and no state-filling is observed. This notion is further corroborated by the near-identical E_{11}*/E_{11} peak ratios as shown in Figure S11, suggesting similar excitation density regimes in EL and non-resonant (785 nm cw excitation) PL experiments.
Figure S17. Schematic setup for charge modulation photoluminescence (CMPL) spectroscopy. SWCNT network FETs are optically excited with a 785 nm laser diode operated in continuous wave mode. The charge carrier density in the FET channel is modulated with a waveform generator by applying a sinusoidal bias (offset voltage, $V_{os}$; peak-to-peak voltage, $V_{pp}$) to the gate electrode. The emission is spectrally resolved and the signal is detected with an InGaAs photodiode. A lock-in amplifier, which is fed with the sinusoidal bias from the waveform generator, recovers the differential change in PL ($\Delta PL$) by phase-locking the photodiode signal to the reference signal.
Figure S18. a) Normalized voltage-dependent CMPL spectra (absolute intensities shown in Figure 5a of the main text) of a pristine (6,5) SWCNT network (modulation frequency $f = 363$ Hz, peak-to-peak voltage $V_{pp} = 0.2$ V). b) Frequency-dependent CMPL spectra of a pristine SWCNT network and c) spectra normalized to the E$_{11}$ $\Delta$PL signal. The nearly identical normalized spectra confirm the common physical origin (i.e., quenching by mobile charges) of the peaks.

Figure S19. a) Frequency-dependent CMPL spectra of an sp$^3$-functionalized SWCNT network with high defect density and b) spectra normalized to the E$_{11}$ $\Delta$PL signal. The nearly identical normalized spectra confirm the common physical origin (i.e., quenching by mobile charges) of the peaks.
Figure S20. **a)** Voltage-dependent CMPL spectra of a sp³-functionalized SWCNT network with low defect density (modulation frequency $f = 363$ Hz, peak-to-peak voltage $V_{pp} = 0.2$ V) and **b)** spectra normalized to the $E_{11}$ $\Delta$PL signal. **c)** Frequency-dependent CMPL spectra of an sp³-functionalized SWCNT network with low defect density and **d)** spectra normalized to the $E_{11}$ $\Delta$PL signal. The nearly identical normalized spectra confirm the common physical origin (i.e., quenching by mobile charges) of the peaks.
Temperature-Dependent Electrical Characterization of SWCNT FETs

Extraction of Trap Densities from the Subthreshold Regime

Figure S21. Zoom-in on the subthreshold regime in the transfer characteristics (source-drain voltage $V_{ds} = -100$ mV, $T = 300$ K) of pristine and sp$^3$-functionalized SWCNT network FETs (drain currents, solid lines; gate leakage currents, dashed lines).

As detailed by Kalb et al. the relation between the subthreshold swing $S$ and the trap density $N_o$ is given by the following formula:\(^7\)

$$S = \frac{k_B T \ln(10)}{e} \left(1 + \frac{e^2}{C_i} N_o \right) = \frac{\partial V_g}{\partial (\log(I_d))}$$

(1)

In Equation (1), $k_B$ is the Boltzmann constant, $T$ is the temperature, $e$ is the elementary charge, and $C_i$ is the areal capacitance. The calculated values for the trap densities are provided in Table S2.
**Table S2.** Trap density for holes and electrons calculated from the subthreshold slopes of the transfer characteristics of pristine and sp³-functionalized SWCNT network FETs shown in Figure S21 according to Equation (1).

|                | Trap density for holes $N_{\square}(h^+) \text{ (cm}^{-2} \text{ eV}^{-1})$ | Trap density for electrons $N_{\square}(e^-) \text{ (cm}^{-2} \text{ eV}^{-1})$ |
|----------------|-------------------------------------------------------------------------------------------------|-----------------------------------------------------------------|
| Pristine       | $(5.9 \pm 0.3) \cdot 10^{12}$                                                                 | $(10.1 \pm 0.1) \cdot 10^{12}$                                  |
| Low defect density | $(8.3 \pm 0.3) \cdot 10^{12}$                                                              | $(13.1 \pm 0.1) \cdot 10^{12}$                                  |
| High defect density | $(9.4 \pm 0.3) \cdot 10^{12}$                                                                | $(16.0 \pm 0.1) \cdot 10^{12}$                                  |

**Schematic Device Layout and Principle of Gated Four-Point Probe Measurements**

**Figure S22.** Working principle of gated four-point probe measurements. As shown in the schematic device layout (layers are laterally shifted and scaled for better visibility), two voltage probes ($V_{P1}$, $V_{P2}$) are defined at the positions $L_1 = 8 \, \mu\text{m}$, $L_2 = 32 \, \mu\text{m}$ within the channel ($L = 40 \, \mu\text{m}$). By linearly extrapolating the potential gradient in the transistor channel measured with the voltage probes (solid line), the potential drops at the source and drain electrodes ($\Delta V_s$, $\Delta V_d$) are determined and thus the contact resistance can be calculated. $\Delta V_{\text{ch}}$ is the actual channel potential, and the dashed line corresponds to an ideal case without any contact resistance.
Temperature-Dependent Mobilities

Figure S23. Full dataset of temperature-dependent, contact resistance-corrected linear mobilities of pristine and sp³-functionalized SWCNT network FETs. Graphs show a, b) absolute and c, d) normalized mobilities in the hole and electron transport regimes, respectively. For better comparison, all values were extracted at a fixed gate voltage overdrive of ±6 V for electrons and holes, respectively.
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