Raman Measurements on Electrochemically Doped Single-Walled Carbon Nanotubes

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Abstract. We performed voltammetry experiments and studied the Raman response of electro-chemically doped single-walled carbon nanotubes (SWNT) using different salt solutions. The frequency shift of the radial breathing mode (RBM) and the high-energy mode (HEM) were examined as a function of the doping grade. The results are discussed in the frame of a double-resonant model for Raman scattering and a strain estimate from the the high-energy mode shift is proposed.

Introduction. Single-wall carbon nanotubes (SWNT) are novel one-dimensional nanostructures with promising application perspectives. Along with their remarkable electronic properties they combine large surface area, good chemical stability and significant elastic properties[1, 2]. The SWNTs exhibit sharp optical transitions between van Hove singularities in their electronic density of states. Consequently, any charge-transfer doping should lead to significant changes in the electronic properties. A high-degree charge transfer can be achieved by intercalation as the guest species move into the interstitial channels of the SWNT ropes, however, much finer tuning of the added charge is achieved by electrochemical doping[3]. In the latter case the electrolyte ions do not seem to penetrate the SWNT ropes at mild potentials. They rather seem to form a charged double layer only with the external surface of the ropes. Our results support the evidence that in aqueous solutions at potentials up to +1 V (*p*-doping) SWNT ropes participate only with their external surface in the double-layer charging. We further propose an electrochemical way to determine the effective surface area of SWNT electrodes. We also relate the electrochemically induced shift of the high-energy mode (HEM) frequency to the dimensional changes of the SWNTs and discuss the Raman response in terms of the double-resonant scattering model[4].

Experimental. A stripe of SWNT paper with diameter distribution ranging from 1.2 nm to 1.4 nm was prepared as a working electrode in a three-electrode cell equipped with quartz windows. A detailed characterization of the sample can be found in Ref. 2. A Metrohm - Potentiostat was employed for cyclic voltammetry measurements. A platinum wire and Ag/AgCl/3 M KCl served as auxiliary and reference electrode, respectively. The working electrode was only partly dived into the solution and was electrically contacted at its dry end.

Several different aqueous solutions (concentration 1 M) were applied in the voltammetric measurements: LiCl, NaCl and KCl. Each solution was purged with N_2 gas prior to measurements to remove excessive oxygen. The Raman spectra were recorded with a
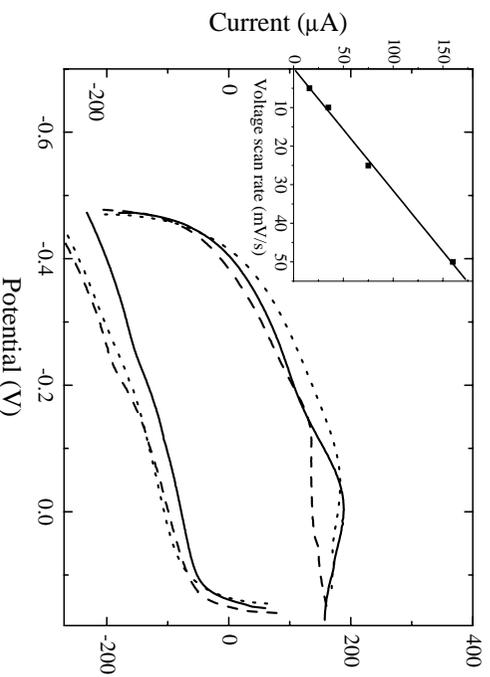
FIGURE 1. Cyclic voltammograms of a 1 mm² SWNT-mat in 1 M aqueous solutions of LiCl (full line), NaCl (dashed line) and KCl (dotted line) at a scan rate of 50 mV/s; all potentials are vs Ag/AgCl. *Inset:* Saddle-point current of the voltammogram for KCl as a function of the voltage scan rate.

DILOR triple grating spectrometer equipped with a CCD detector. The 514.5 nm line of an Ar^+/Kr^+ laser was used and the spectral resolution was 4 cm^{-1}.

Results and Discussion.

Figure 1 shows typical cyclic voltammograms of a SWNT electrode. Regarding the sample approximately as a double-layer capacitor and taking for the current values the saddle points of the upper and lower curves, respectively, we estimated gravimetric capacitances in the range 33 - 38 F/g for the three solutions used which are in line with the ones reported in the literature[2, 3].

We also propose an electrochemical method to determine the effective surface area by means of a glassy carbon rod as a working electrode. A glassy carbon electrode has a smooth shiny surface without any pores which equals its effective surface area in a voltammetric experiment. By putting the measured currents in proportion for both glassy carbon and SWNT electrodes one can therefore determine the effective surface area of the SWNT sample. In this way we obtained similar values of $\approx$230 m²/g for all three solutions that are slightly smaller than those measured by the conventional N$_2$ absorption method (285 m²/g)[2]. The ratio between our measured values and theoretical estimates for individual nanotubes (1315 m²/g) is $\approx$ 0.175, which implies that the nanotube bundles are involved in the double-layer charging only with their external area and that the majority of these bundles contain about 90 nanotubes. The latter value is in good agreement with TEM results[5], which revealed bundles made of 100 nanotubes in average.

We further recorded Raman spectra of the main vibrational modes from the SWNT working electrode at different constant potentials in all three chloride solutions. The recorded spectra (KCl solution) and the phonon frequencies versus applied voltage are shown in Fig. 2 for the RBM and in Fig. 3 for the two most intense peaks of the HEM. It is apparent that up to $\approx$ 1 V the frequency shift scales linearly with the applied voltage. We measured the RBM frequency of the original SWNT mat, and of
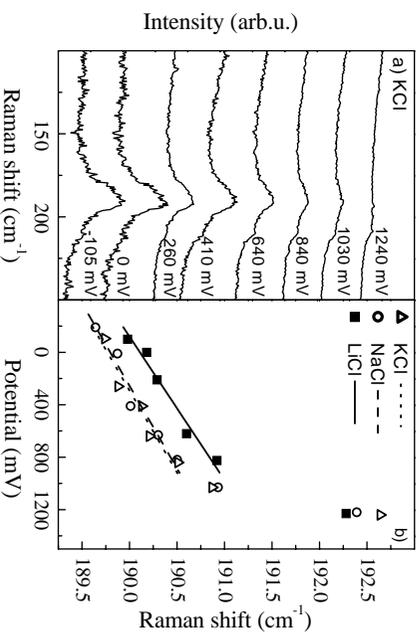
a) KCl

Intensity (arb.u.)

1240 mV
1030 mV
840 mV
640 mV
410 mV
260 mV
105 mV
0 mV

Raman shift (cm⁻¹) 150 200

b)

KCl ······ △
NaCl – – – ○
LiCl —— ■

Potential (mV) 0 400 800 1200

Raman shift (cm⁻¹) 192.5 192.0 191.5 191.0 190.5 190.0 189.5

the SWNT working electrode at open circuit before cycling and immediately after taking the Raman spectra at $U = \pm 1$ V. The obtained values coincided to within 0.2 cm⁻¹ with the original RBM frequency. This along with the small shift of the RBM below 1 V gives us confidence that the ionic species do not significantly penetrate into the SWNT bundles and the effective surface area remains constant. Such a penetration would alter the van-der-Waals interaction strength, which provides an essential contribution to the RBM frequency[6]. At higher voltages the frequency shift increases exponentially. This is accompanied by a similar increase in current which may indicate an onset of intercalation.

From a linear fit to the frequency points (up to 0.8 V, KCl solution) we estimate a doping-induced shift of 160 cm⁻¹/e⁻/C-atom for the RBM, 270 cm⁻¹/e⁻/C-atom for the main HEM peak at 1593 cm⁻¹ (HEM1) and 320 cm⁻¹/e⁻/C-atom for the second-strongest HEM peak at 1567 cm⁻¹ (HEM2) in qualitative agreement to previous results[3]. As can be seen in Fig. 3, the frequency slope of HEM2 is slightly but systematically steeper than that of HEM1. In the framework of the double-resonant model for Raman scattering in SWNT[4] such a slope difference may be accounted for. Shifting the phonon branches to higher frequencies upon doping necessarily decreases the wave vector of the phonon to be emitted. The overall hardening of HEM1 is thus weakened while that of HEM2 is enhanced due to the different dispersion of the two phonon branches originating from the graphitic E_{2g} mode.

The actuation strain ε_{zz} of the SWNTs can be estimated from the average HEM frequency shift $\Delta\omega$ utilizing its linear dependence on the doping grade Δf. Assuming equal deformations along the nanotube axis and in circumferential direction and recalling the analogy to the Grüneisen parameter γ for pressure-induced strain[7], we use here a similar phonon deformation potential of order unity and obtain

$$\frac{\Delta\omega(\Delta f)}{\omega_0} = 2\gamma\varepsilon_{zz}. \tag{1}$$
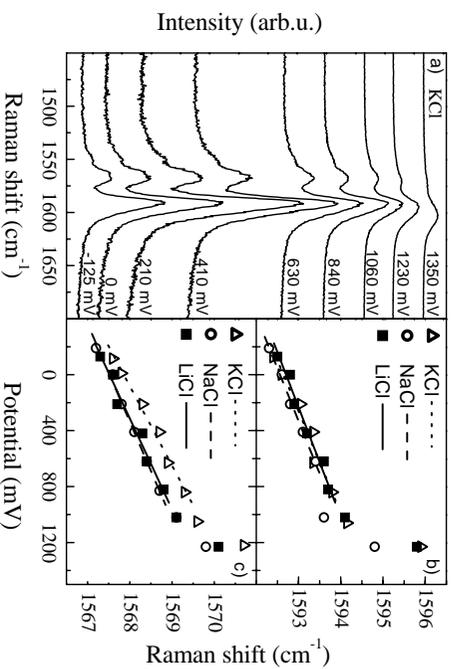
FIGURE 3. *a*) Raman spectra of the high-energy mode (HEM) at several potentials applied to the SWNT-mat (1 M KCl). *b*) The frequency of HEM1 as a function of the applied potential for three different solutions: LiCl (squares), NaCl (circles) and KCl (triangles). *c*) Same as *b*) for HEM2.

Then at ≈ 1 V applied potential the doping grade amounts to $\Delta f \approx 0.005$ e$^-$/C-atom and the strain ε_{zz} to ≈0.05%.

Conclusions. We measured the voltammetric response of a SWNT-paper as a working electrode in an electrochemical experiment, determined its gravimetric capacitance and used a comparative method to estimate its effective surface area with the same experimental setup. We also examined the Raman response of the nanotube vibrational modes upon electrochemical doping in the framework of the double-resonance scattering model. We showed that the high-energy stretching SWNT mode can be used to assess the actuation properties of a carbon nanotube.

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