Raman spectroelectrochemistry on SWNTs at higher doping levels: Evidence for a transition to intercalative doping

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We studied the transition from the electrochemical double-layer charging regime to intercalative doping of SWNT buckypaper in KCl aqueous solution. For this purpose we used doping levels by applying constant potentials above 1 V approaching and slightly exceeding the oxidation potential for Cl⁻ ions. At each potential *in situ* Raman measurements of the radial breathing mode (RBM), the high-energy tangential mode (HEM) and the disorder-induced (D) mode were performed. From a comparative analysis of the Raman spectra we conclude that above 1 V a significant penetration of chlorine species into the interstitial channels of the SWNT bundles and possibly functionalization take place.

1 Introduction

Single-wall carbon nanotubes (SWNT) are remarkable nanostructures with promising perspectives for application as batteries [1], actuators [2] and various electronic devices [3]. Plenty of these applications are related to doping of SWNTs as their electronic and mechanical properties are very sensitive to charge transfer. For instance, the resistivity of a semiconducting SWNT can be varied over many orders of magnitude upon electrostatic gating or gas absorption which implies applications such as SWNT-FETs [4] or electrochemical sensors [5]. This sensitivity, on the other hand, makes Raman spectroscopy a powerful and favored tool to examine doping-induced phenomena.

There are several ways to dope carbon nanotubes. A high degree of charge transfer can be achieved by intercalation, as the guest species in the interstitial channels form a stable charge-transfer compound with the SWNT ropes [6]. On the other hand, a finer tuning of the added charge in the SWNTs can be accomplished electrochemically by varying the potential at their contact interface with an electrolytic solution [2, 7, 8]. In this case, the electrolyte ions do not readily penetrate the SWNT ropes. Instead, during the initial stages of electrochemical doping, they form a charged double layer only with the external surface of the ropes [7, 9]. This is of key importance for the SWNT application as actuators, because SWNT expansion or contraction can be related to the transferred charge, which in the double-layer model can be calculated from the applied voltage [7].

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Functionalization provides a combination of doping with selective modification of a variety of chemical properties of SWNTs. Attachment of appropriate functional groups dramatically increases the solubility of the nanotube material [10]. Organic molecules can be coupled with functionalized nanotubes for sensor applications. Specific functionalization involving covalent bonds can create cross-links between SWNTs to form complex nanotube networks [10]. However, covalent bonds lead to a localization of the nanotube electronic states thus lowering the concentration of free charge carriers in contrast to doping.

Electrochemistry is a convenient tool to study doping and functionalization, as it can be applied in both the double-layer and the intercalative regime and can be applied for adsorption and covalent bonding [11–13] as well, depending on the electrolyte species. Here we report an *in situ* Raman investigation of the electrochemical response of SWNT ropes exposed to higher potentials that cause faradeic current and electrolytic reactions. We argue that these processes lead to intercalation and functionalization of the SWNT which can be monitored by Raman spectroscopy.

2 Experimental

A stripe of SWNT "buckypaper" with a nanotube diameter distribution ranging from 1.25 nm to 1.45 nm and a surface density of about 10^{-5} g/mm^2 was prepared as a working electrode in a three-electrode cell equipped with quartz windows for *in situ* spectroscopic control. The measurements were carried out using a Metrohm Three-Electrode-Potentiostat. A platinum wire and Ag/AgCl/3 M KCl served as auxiliary and reference electrode, respectively. The working electrode was electrically contacted at its end and was partly dipped into the solution (dipped part of $\approx 2–3$ mm^2 in 1 M aqueous solution of KCl). The double-layer capacitance of the working electrode was measured by cyclic voltammetry [9] and found to be about 35 F/g. At the beginning of the measurement series the working electrode was cycled several times between 0.4 and -0.4 V to ensure a maximum degree of wetting and to remove oxygen-containing functionalities possibly adsorbed on the SWNT sidewalls. The electrolyte solution was purged with N$_2$ gas prior to the measurements to remove dissolved oxygen. All chemicals used were of analytical grade quality. The solutions were prepared using doubly destilled water.

The nanotube electrode was polarized anodically in order to utilize the relatively low oxidation potential of the chloride ions (1.36 V). Oxidation of the OH$^-$ ions on carbon electrodes in alkali choride solutions is normally shifted to higher potentials due to a high overvoltage. Therefore one can safely assume that possible electrolytic reactions at potentials of $1.2–1.5$ V comprise predominantly oxidation of Cl$^-$. Above 1200 mV a formation of gas bubbles commenced with increasing strength which caused large noise and suppressed the signal so it became impossible to proceed with the Raman monitoring above 1500 mV. Due to the significant cell current flowing above 1000 mV, the exact determination of the applied potential was difficult, therefore from 1100 mV the cell was operated in galvanostatic mode.

The Ar$^+$Kr$^+$ laser line at 1.92 eV was used for excitation. The Raman spectra were recorded *in situ* with a DILOR triple grating spectrometer equipped with a CCD detector. The spectrometer was calibrated in frequency using a Neon lamp and the laser plasma lines.

3 Results and discussion

Figure 1 shows Raman spectra of the radial breathing mode (RBM), the disorder-induced (D) mode and the high-energy mode (HEM) at several elevated potentials, i.e. doping levels. In Fig. 2(a)–(c) the frequency dependence of these modes is presented as a function of the applied potential. Initially, all frequencies exhibit only slight linear upshifts with doping up to 700 mV, except the resonantly enhanced features from metallic SWNTs on the low-energy side of the HEM band, which are very sensitive to doping [14]. This behavior is well described within the double-layer charging model of electrochemical doping. However, upon further potential increasing all modes undergo strongly non-linear jumps in frequency and intensity. The HEM undergoes a dramatic intensity redistribution connected with replacing of the main HEM peak P1 at ≈ 1585 cm^{-1} by a new one P0 at ≈ 1595 cm^{-1} which is absent in undoped SWNTs. The drop in RBM frequency and intensity signals a weakening of the intertube van der Waals
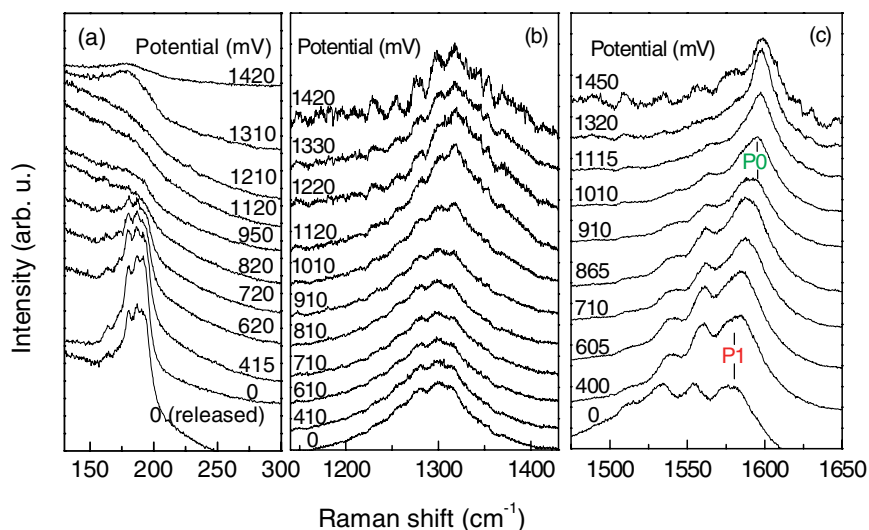
Fig. 1 (online colour at: www.pss-b.com) Raman spectra at 1.92 eV excitation energy of the radial breathing mode (a), the disorder-induced mode (b) and the high-energy mode (c) at several elevated potentials.

coupling which significantly contributes to the RBM force constant [15]. This normally occurs upon penetration of intercalating species into the SWNT bundles. The HEM shape above 1200 mV resembles that of intercalated or functionalized [16, 17] SWNTs. As both peaks P0 and P1 coexist in the HEM between 800 mV and 1200 mV, P0 gaining intensity from P1, our tentative explanation is that P0 develops from P1 in tubes that have undergone functionalization. The increase in the D-mode intensity (Fig. 2(f)), which is proportional to the defect density, may also signal functionalization of the SWNTs.
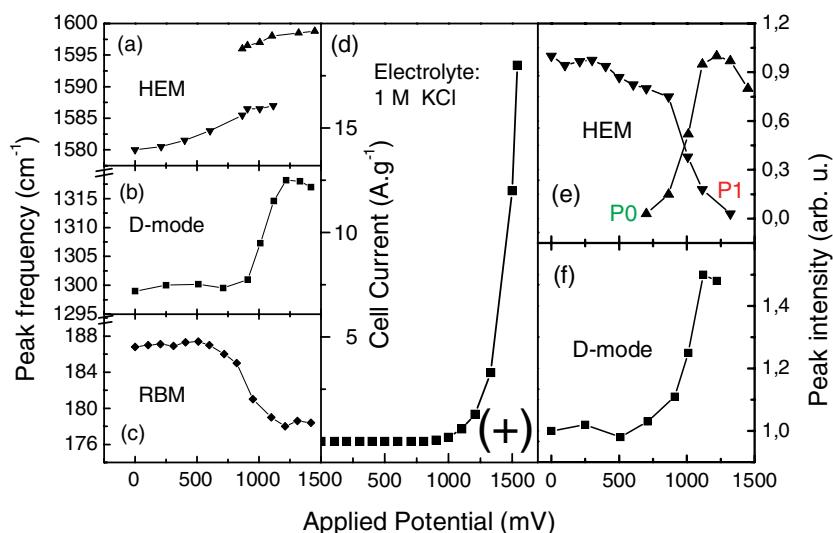

Fig. 2 (online colour at: www.pss-b.com) (a)–(c) Comparative plot of the doping-induced frequency shifts of the HEM (a), the D-mode (b) and the RBM (c) showing a strong correlation in their doping response. (d) The specific current flowing through the electrochemical cell vs. the applied potential in anodic polarization (+). (e) Integrated intensities of the HEM peaks P0 and P1 vs. the applied potential. (f) Integrated intensity of the D-mode vs. the applied potential.

All these changes take place in a strongly correlated manner as shown in Fig. 2(a)−(f) and correspond to the onset of a significant cell current which start to exponentially increase between 800 mV and 1200 mV as shown in Fig. 2(d). As the oxidation potential for Cl⁻ ions in aqueous KCl is relatively low, we expect this current to comprise transport of Cl⁻ ions towards the anode. Upon discharging the most part of the newly created Cl molecules emerge as gas bubbles. However a bundle penetration and adsorption of even a small amount of chlorine species onto the nanotube walls can cause a much larger charge transfer than is possible with double-layer charging which can explain the presented Raman observations. This explanation is additionally supported by the fact that the nonlinear changes first appear in the behavior of the RBM mode which reverse its linear upshift into a downshift already at about 600 mV (see Fig. 2(c)) thus signaling a possible onset of penetration into the bundles. The intensity increase of the D-mode is the latest process which starts when the potential exceeds 1000 mV (Fig. 2(f)), and may reflect formations of new chemical bonds.

4 Conclusions

At potentials above 1 V in aqueous chloride solutions a penetration of chlorine species begins into the interstitial channels of bundled SWNTs and an electrochemical functionalization [12, 13] of the SWNTs is possible. The onset and the initial stages of this penetration can be monitored by Raman spectroscopy and possibly controlled after a suitable calibration to the Raman intensity.

References

[1] A. S. Claye, J. E. Fisher, C. B. Huffman, A. G. Rinzler, and R. E. Smalley, J. Electrochem. Soc. **147**, 2845 (2000).
[2] R. H. Baughman, C. Cui, A. Zakhidov, Z. Iqbal, J. N. Barisci, G. M. Spinks, G. G. Wallace, A. Mazzoldi, D. D. Rossi, A. G. Rinzler et al., Science **284**, 1340 (1999).
[3] S. Reich, C. Thomsen, and J. Maultzsch, Carbon Nanotubes: Basic Concepts and Physical Properties (Wiley-VCH, Weinheim, 2004).
[4] S. J. Tans, A. Verschueren, and C. Dekker, Nature (London) **393**, 6680 (1998).
[5] A. Modi, N. Koratkar, E. Lass, B. Wei, and P. M. Ajayan, Nature (London) **424**, 171 (2003).
[6] A. M. Rao, P. C. Eklund, S. Bandow, A. Thess, and R. E. Smalley, Nature (London) **388**, 257 (1997).
[7] L. Kavan, P. Rapta, L. Dunsch, M. J. Bronikowski, P. Willis, and R. Smalley, J. Phys. Chem. B **105**, 10764 (2001).
[8] C. P. An, Z. V. Zardeny, Z. Iqbal, G. Spinks, R. H. Baughman, and A. Zakhidov, Synth. Met. **116**, 411 (2001).
[9] M. Stoll, P. M. Rafailov, W. Frenzel, and C. Thomsen, Chem. Phys. Lett. **375**, 625 (2003).
[10] U. Dettlaff-Weglikowska, J.-M. Benoit, P.-W. Chiu, R. Graupner, S. Lebedkin, and S. Roth, Current Appl. Phys. **2**, 497 (2002).
[11] A. Claye, J. E. Fischer, and A. Metrot, Chem. Phys. Lett. **330**, 61 (2000).
[12] J. L. Bahr, J. Yang, D. V. Kosynkin, M. J. Bronikowski, R. E. Smalley, and J. M. Tour, J. Am. Chem. Soc. **123**, 6536 (2001).
[13] E. Unger, A. Graham, F. Kreupl, M. Liebau, and W. Hoenlein, Curr. Appl. Phys. **2**, 107 (2002).
[14] P. M. Rafailov, J. Maultzsch, C. Thomsen, and H. Kataura, Phys. Rev. B **72**, 045411 (2005).
[15] C. Thomsen, S. Reich, A. R. Goni, H. Jantoljak, P. M. Rafailov, I. Loa, K. Syassen, C. Journet, and P. Bernier, phys. stat. sol. (b) **215**, 435 (1999).
[16] V. Skakalova, A. B. Kaiser, U. Dettlaff-Weglikowska, K. Hrncarikova, and S. Roth, J. Phys. Chem. B **109**, 7174 (2005).
[17] U. Dettlaff-Weglikowska, V. Skakalova, R. Graupner, S. H. Jhang, B. H. Kim, H. J. Lee, L. Ley, Y. W. P. S. Berber, D. Tomanek, and S. Roth, J. Am. Chem. Soc. **127**, 5125 (2005).