

## ELECTROCHEMICAL CHARGING OF SINGLE WALLED CARBON NANOTUBES: AN IN-SITU RAMAN SPECTROELECTROCHEMICAL STUDY

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In-situ Raman spectroelectrochemistry is a well established method to study the electronic structure of carbon nanostructures such as SWCNTs, DWCNTs and peapods. In contrast to chemical doping, electrochemistry allows a precise and well controlled doping of carbon nanostructures. The Raman spectra of SWCNTs are resonantly enhanced and thus by selection of the appropriate laser excitation energy an array of tubes is chosen which appear in the spectra. This allows a study of the effects of doping on metallic or semiconducting tubes in a separate way, even if the tubes are mixed in a sample. Recently, a number of spectroelectrochemical studies of SWCNTs was published both on bundles and individual tubes, which confirm the importance of Raman spectroelectrochemistry for the evaluation of the changes in electronic structure of carbon nanotubes upon doping. In general, the doping (electrochemical charging) of SWCNTs leads to a shift of the Fermi level. When the Fermi level reaches the energy of the Van Hove singularity, it suppresses the electronic transitions from/to this particular singularity. If the Raman signal is in resonance with this optical transition including such a singularity ( $E_{ii}^R$ ) a strong bleaching of the Raman intensity for this feature is expected. However, we have recently shown that this simple model must be revisited.<sup>[1]</sup>

We have inspected the Raman spectra of SWCNTs during electrochemical doping and focused the study on the detailed development of the radial breathing mode (RBM) of SWCNTs under precise control of the electrochemical charging. We show that the RBM band is changed already at early stages of the electrochemical doping, well before the Fermi level of the electrode reaches the energy of the Van Hove singularity which is responsible for resonance enhancement (optical transition  $E_{ii}^R$ ). The intensity of the RBM changes for both the semiconducting and metallic tubes, but the dependence on the electrode potential has been found to be different for metallic and semiconducting tubes, due to the different electronic structure of these types of carbon nanotubes.

We found that the bleaching of the RBM band starts to occur at the potential where the first available electronic states are affected. This happens when the potential is changed from  $E = 0$  V (in case of metallic tubes) or with a delay of about 0.5 or -0.5 Volts (in case of semiconducting tubes). It is important to emphasize that this in contrast to the general assumption that the spectra should be affected only if the Fermi level reaches the energy of the Van Hove singularity which is in resonance with excitation laser energy. Therefore, even at a low level of doping, significant changes in the electronic structure of carbon nanotubes occur and the electronic states cannot be considered as rigid if the SWCNTs are doped. The electronic conditions at the electrode surface with a nanotube layer are discussed in detail.

[1] M. Kalbac, L. Kavan, L. Dunsch. *J. Phys. Chem. C* **2008**, 112(43), 16759-16763.