Charge Transfer at Carbon Nanotubes with Encapsulated C_{60}/C_{70} (Peapods)

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Charger-transfer on fullerene peapods (C_{60}@SWCNT[1] and C_{70}@SWCNT) was studied by electrochemistry in 0.2 M $LiClO_4$ + acetonitrile. This strategy allows easy and precise control of the population of electronic states between about ± 1.5 eV *vs.* the Fermi level[1-3]. As both the individual components of peapods, i.e. SWCNT and C_{60}/C_{70}, show specific redox response, there is a clear challenge of addressing fundamental problems of charge transfer in nanocarbons.

Electrochemistry of peapods is dominated by capacitive double-layer charging, analogous to that of empty tubes (SWCNT)[2,3]. The reduction of intra-tubular C_{60}/C_{70} is hampered; hence, no fullerene-related faradaic processes are detectable.

Vis-NIR spectroelectrochemistry points at reversible and fast bleaching of the electronic transitions between Van Hove singularities[2,3], which also causes reversible quenching of resonance Raman scattering of both radial breathing (RBM) and tangential (TM) modes of SWCNT[2,3]. Cathodic charging of C_{60}@SWCNT leads to bleaching of the C_{60} Raman modes, but this effect is, surprisingly, not mirrored upon anodic charging (Fig. 1). The electrochemical charging influences preferentially the peapod wall, causing the depletion/filling of states close to the Fermi level of SWCNT. This manifests itself by symmetric anodic/cathodic bleaching of the RBM/TM modes and the corresponding frequency shifts.

The asymmetric response of C_{60}-peas is caused by the fact that the Fermi level of SWCNT is close to LUMO of C_{60} (t_{1u}). For cathodic polarization, electrons are transferred from the wall to the LUMO of C_{60}-peas. Hence, the HOMO-LUMO transition C_{60}-peas is suppressed, and the resonance Raman scattering is quenched too. However, the anodic depletion of valence band does not influence the electronic transitions of C_{60}-peas. Consequently, the excitation of C_{60}-peas is allowed at all potentials above the Fermi level. As the tube-related modes decline monotonously upon both cathodic and anodic charging, the strongest C_{60}-related mode, $A_g(2)$ becomes dominant over the tube-related modes at highly positive potentials. Anodic charging also allows a disclosure of the $H_g(8)$ line, due to the frequency up-shift of the TM mode. This is interesting, since the $H_g(8)$ mode cannot be observed in dry peapod, due to overlap with strong TM features.

The C_{70}@SWCNT exhibits qualitatively different behavior. The most striking feature is, that the "anodic enhancement" of Raman scattering from C_{60}-peas is not reproduced in C_{70}@SWCNT. All the relevant modes of C_{70}-peas show the "normal" symmetric charge-transfer bleaching as the RBM/TM lines. Analogously to C_{60}@SWCNT, electrochemical charging allows detecting of some lines, which are normally hidden by overlapping D- and G-modes of SWCNT.

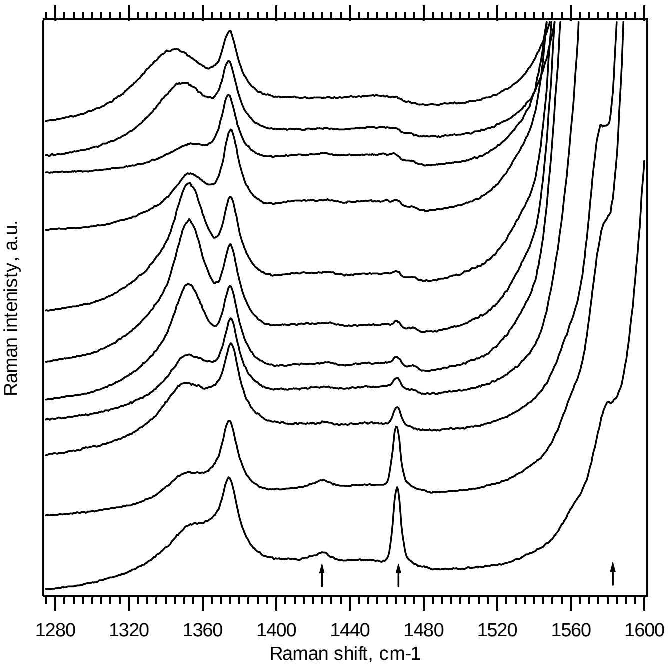

Figure 1 Potential dependent Raman spectra of C_{60}@SWCNT (peapods) on Pt electrode (excited at 2.54 eV) in 0.2 M $LiClO_4$ + acetonitrile. The electrode potential varied by 0.3 V from -1.23 V to 1.77 V vs. Fc/Fc^+ for curves from top to bottom. Spectra are offset for clarity, but the intensity scale is identical. Arrows indicate the expected Raman lines of C_{60}: $H_g(7)$, $A_g(2)$ and $H_g(8)$. Note that the $H_g(8)$ peak is disclosed via a blue shit of the TM mode, which is due to anodic polarization. The peak at 1374.5 cm^{-1} belongs to acetonitrile.

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References

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