RAMAN SPECTROSCOPY OF CARBON NANOTUBES WRAPPED WITH SINGLE- OR DOUBLE-STRANDED DNA OR SURROUNDED BY N-METHYLPYRROLIDONE MOLECULES: COMPARISON OF D AND G BANDS

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Due to exceptional electrical conductivity, high surface area, and sensitivity to local chemical environments, single-walled carbon nanotubes (SWNTs) offer a highly effective platform for biosensing based on electrical properties. SWNTs can form percolated networks or thin films. These networks create interconnected pathways for charge transport, which makes them perspective for label-free electronic biosensing. A target molecule that binds to the functionalized SWNT via the probe causes a change in the charge distribution or local dielectric environment, which can be detected as a shift in electrical resistance, current, capacity, or in the Raman spectrum. Raman spectra of nanotubes are extremely sensitive to changes in the external environment, which manifest themselves in changes in the position, shape, and intensity of characteristic bands of nanotubes.

In this work, the vibrational structure of SWNTs wrapped with single- or double-stranded DNA (ssDNA/dsDNA) or surrounded by N-methylpyrrolidone (NMP) molecules is studied by Raman spectroscopy. Nanotubes were sprayed from aqueous (with DNA) or NMP suspensions on quarts substrates. Raman spectra were recorded in the range of 1000-1700 cm^{-1} in which bands assigned to a tangential (G) and defect (D) modes are observed.

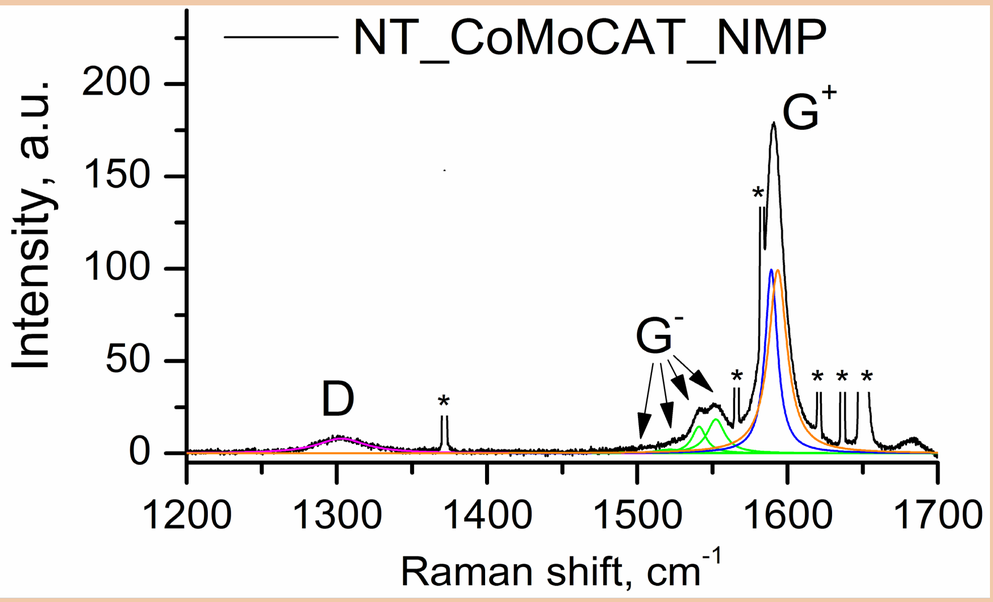

Fig. 1. Raman spectrum of SWNTs deposited from an NMP suspension on a quartz substrate in the range of D and G modes (black). The spectrum was obtained at He-Ne laser excitation (632.8 nm). Symbols * denote laser plasma lines.

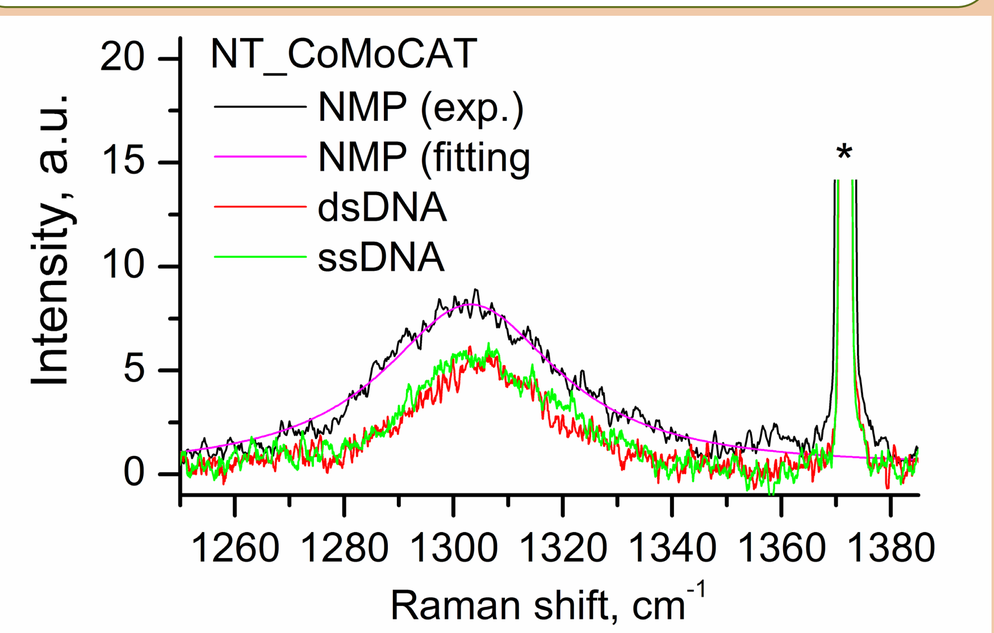

Fig. 2. D mode region of Raman spectra of SWNTs networking deposited from an NMP suspension, aqueous suspensions with ssDNA or dsDNA. Spectra were normalized to the intensity of the G^+-band of the SWNT:NMP spectrum.

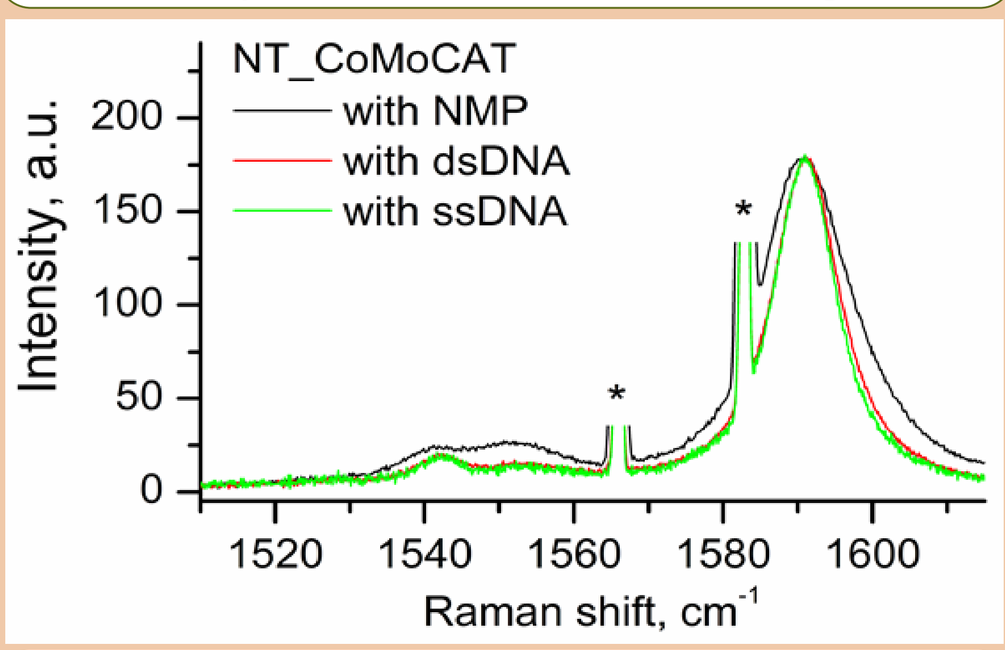

Fig. 3. Tangential mode region of Raman spectra of SWNTs networking obtained from an NMP suspension, ssDNA, and dsDNA aqueous suspensions.

Mode	Frequency of peak, cm^{-1}			FWHM, cm^{-1}			Area, a.u.		
	NMP	dsDNA	ssDNA	NMP	dsDNA	ssDNA	NMP	dsDNA	ssDNA
G^-	1493.1	1493.1	1493	19.9	17.9	16	21.1	39	35.2
--	1522	1523.2 (+1.2)	1523.3 (+1.3)	23	21.5	18.4	77.1	110.7	125.2
--	1541.1	1541.9 (+0.8)	1542 (+0.9)	11.3	7.9 (-3.4)	7.3 (-4.0)	258.3	165	154.4
--	1552.3	1553.6 (+1.3)	1554.1 (+1.8)	14.3	16.8	16.5	416.1	259.5	224.1
G^+	1589.2	1589.9	1590	9.9	9.9	9.8	1551.7	1585.1	1796
	1593.5	1592.5	1592.4	14.8	9.9	8.6	2313	1371	967

- The D-band of the SWNTs:NMP spectrum is more intensive and broader than the D bands of the SWNTs:ssDNA and SWNTs:dsDNA spectra.
- The D band of the SWNTs:NMP sample is softened by 1.9 cm^{-1} compared with the D-band of the spectrum of the SWNTs covered by DNA.
- The difference in Lorentzian parameters between D bands of SWNTs:ssDNA and SWNTs:dsDNA samples is very small, the peak positions are almost the same, the width of the D-band is slightly smaller for the second sample, and the total intensity is also weaker for this sample.

D band

- **Bundling**: NMP broadening, increase of intensity.
- DNA **wrapping:** decrease of intensity.
- **Local strain:** for DNA wrapped SWNTS, shift to high frequency compared to SWNT:NMP
- **Charge transfer**, NMP is a weak donor-acceptor, DNA is a donor – shift to low frequency compared to SWNT:DNA
- The **dielectric constant** (ε) NMP 32, DNA 3-8, SWNT 3-9. For SWNTs covered by NMP, shift to low frequency compared to SWNT:DNA

G-band

- The G^+ band width in the SWNTs:NMP sample is significantly (~1.4 times) broader compared to those observed in SWNTs:DNA samples.
- Among the samples of DNA-wrapped nanotubes, the G^+ band in the spectrum of SWNTs:dsDNA is slightly broader than that of SWNTs:ssDNA.
- **Bundling**: NMP – broadening
- **Local strain:** for DNA wrapped SWNTS, shift to high frequency
- **charge transfer**, NMP is a weak donor-acceptor, DNA is a donor – shift to low frequency
- The **dielectric constant** (ε) NMP 32, shift to low frequency

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Conclusion

- Raman spectra of SWNTs wrapped with ssDNA, dsDNA, or surrounded by NMP show noticeable differences in the G and D bands, reflecting variations in nanotube–molecule interactions.
- Minimal spectral differences are observed between ssDNA- and dsDNA-wrapped SWNTs networks, although broader G^- and G^+ bands in dsDNA samples indicates partial bundling through weaker binding with nanotube compared to ssDNA.
- SWNTs dispersed in NMP exhibit a D-band approximately twice as intense, broader, and slightly downshifted compared to DNA-wrapped SWNTs, evidencing stronger defect-related scattering.
- Differences in band shifts, intensity, and broadening across samples are attributed to combined effects of bundling, charge transfer, different dielectric environments and stress induced by adsorbed molecules.