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Charge transfer between covalently grafted groups and single-walled carbon nanotubes evidenced by Raman and ellipsometric spectroscopies.

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Introduction :

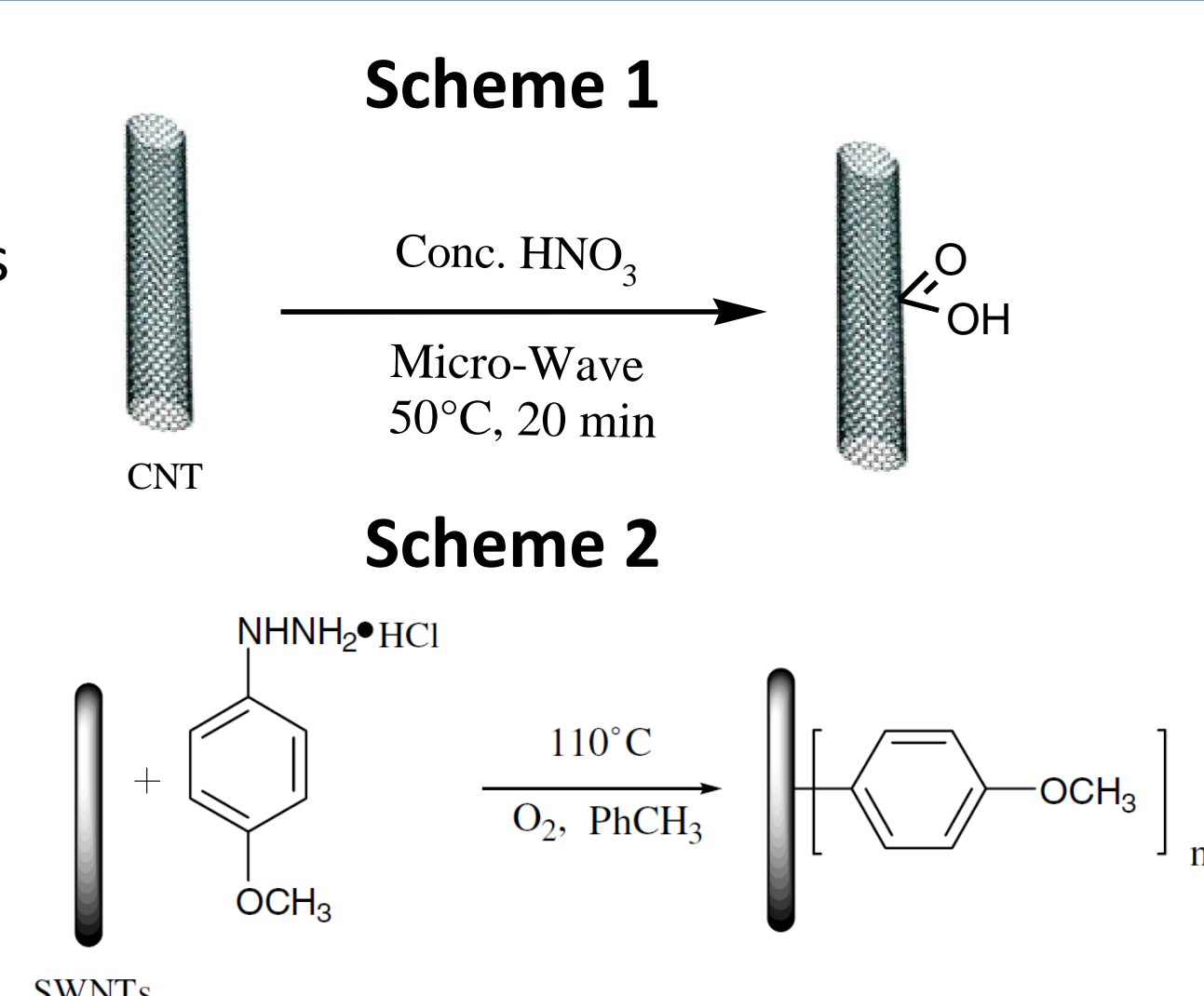
Clean single-walled carbon nanotubes (SWCNTs) synthesized using the HiPCO process and purified (purchased from Nanointegris Inc.) were chemically treated by two different methods: i) a microwave-assisted acidic oxidation process by a concentrated HNO₃ solution (ox-CNTs), ii) a covalent grafting of a methoxyaryl groups by a thermal radical functionalization (MeOB-CNTs). Thin films of raw and chemically modified SWCNTs were made and analysed using ellipsometric spectroscopy from 0.6 to 4.96 eV using three incident angles (50°, 60° and 70°) and also in the infrared region from 0.07 eV to 0.6 eV with a unique incident angle (60°). The films were supposed to be thick and dense enough to model them as a homogeneous and isotropic semi-infinite medium. Under this hypothesis, we analytically calculated the complex dielectric function of the films and extracted the real (ϵ_r) and imaginary (ϵ_i) parts of this function. Raman spectroscopy was also used to assess the number of covalent defects introduced in the graphitic structure of SWCNTs.

Samples

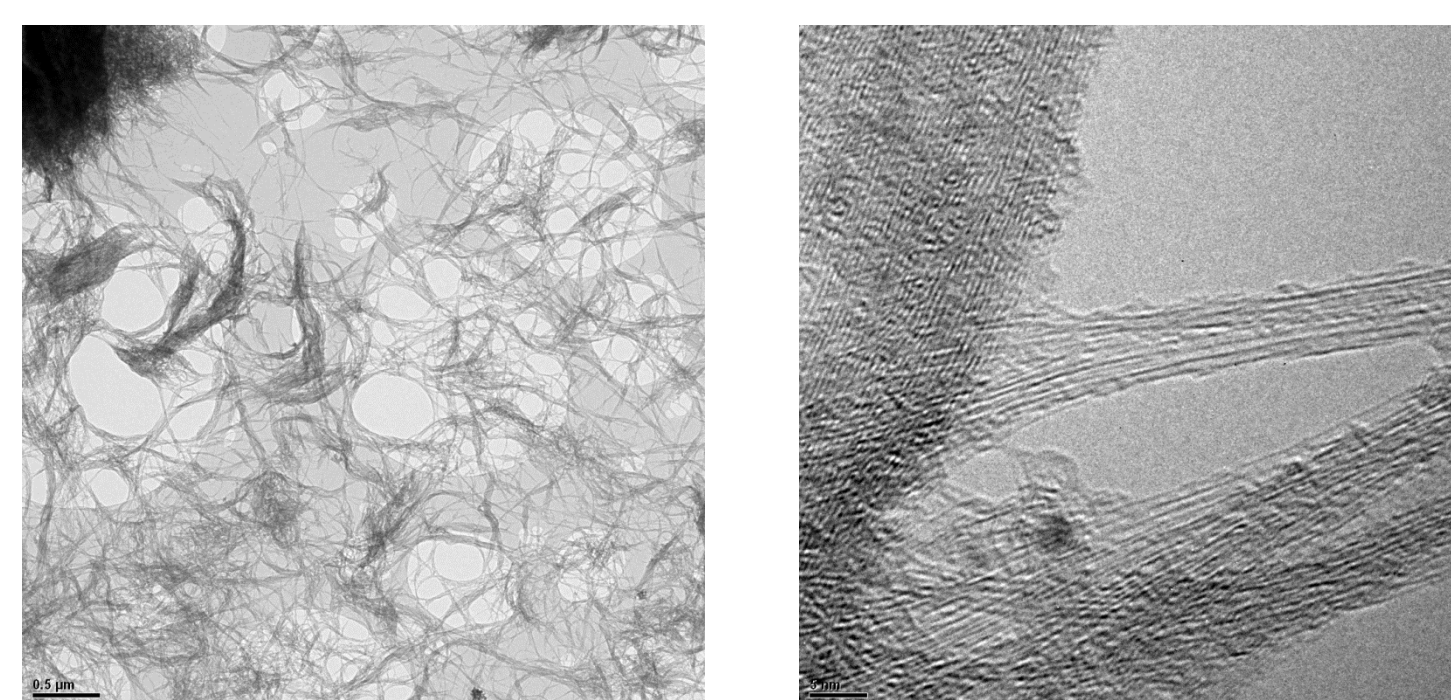
- Super-purified SWCNTs synthesized by HiPCO process (SP-HiPCO from Nanointegris)

- AN276 : SP-HiPCO SP oxidized in HNO₃ 65% under microwave irradiation (20 mn at 400 W), see scheme 1.

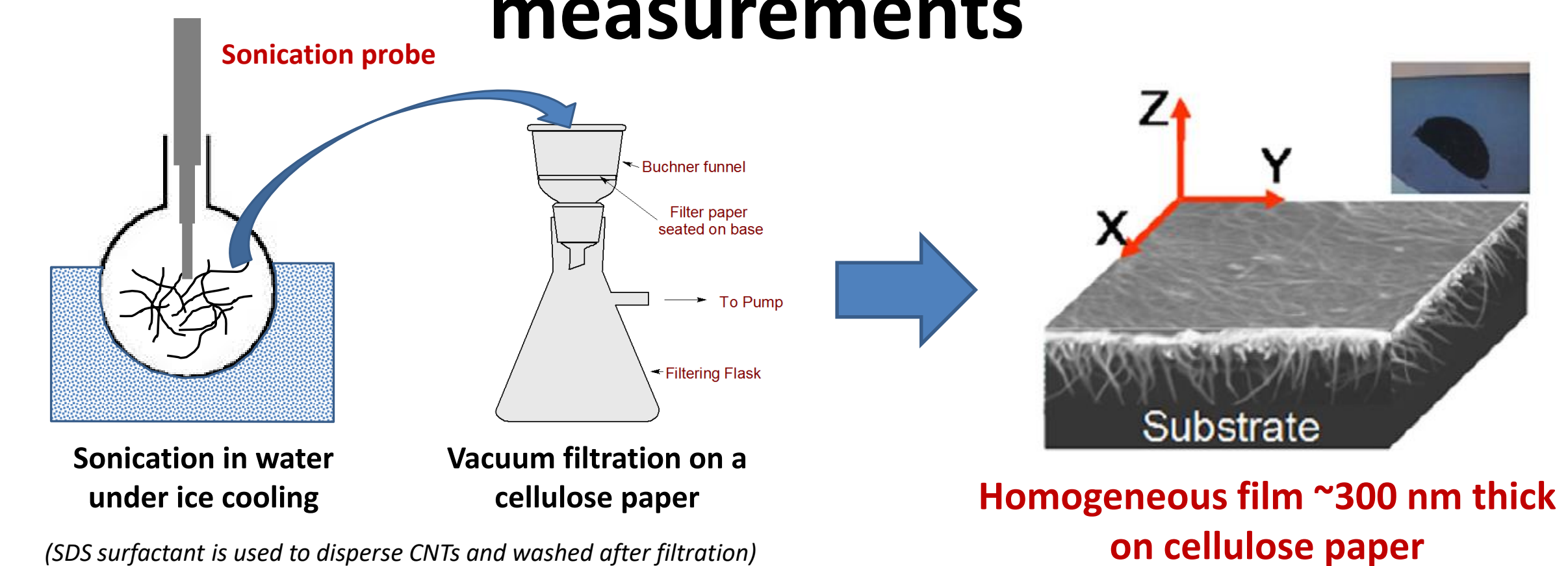
- AN213 : SP-HiPCO SP functionalized with methoxyaryl groups through a radical process (scheme 2).



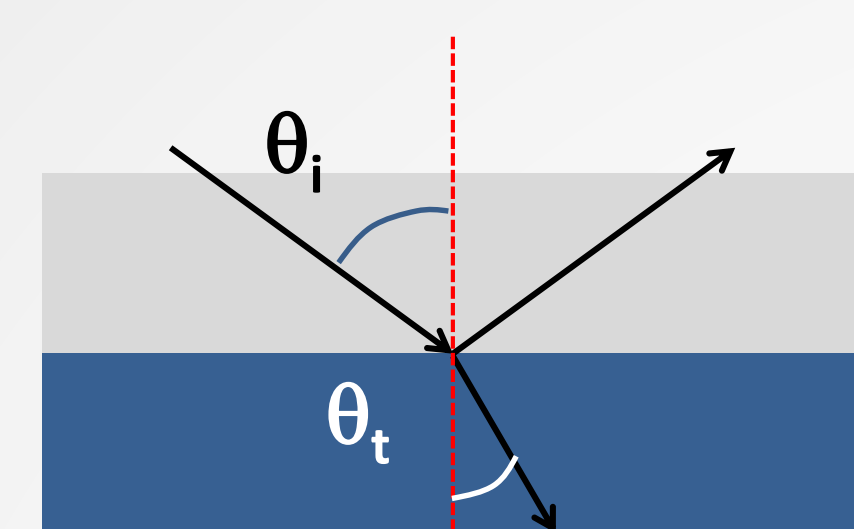
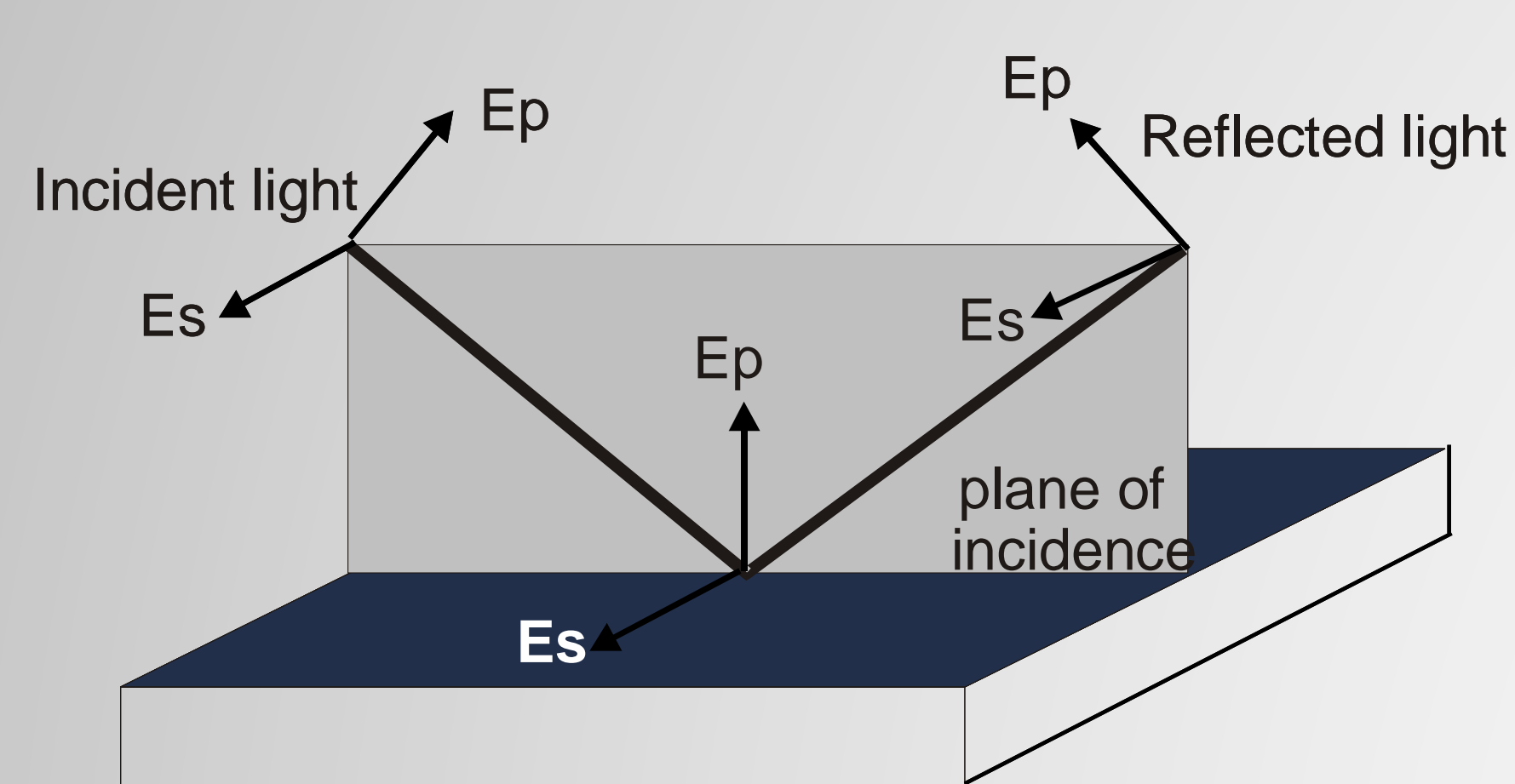
HRTEM micrographs of raw SP-HiPCO sample.



Film preparation for ellipsometric measurements



Spectroscopic Ellipsometry: some definitions



θ_i : 50, 60, 70°

Energy of light: from 0.6 to 4.96 eV and also from 0.07 to 0.6 eV for $\theta_i = 60^\circ$

Fresnel coefficient r_s et r_p

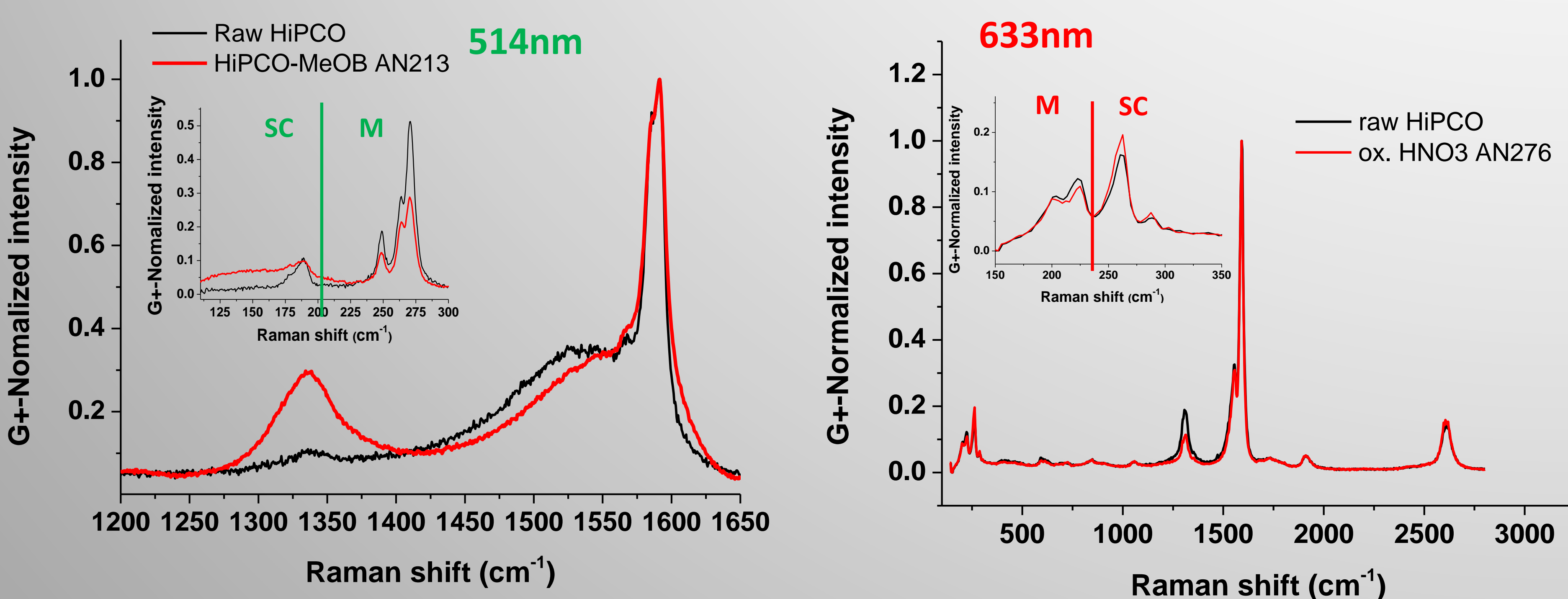
$$r_s = \left(\frac{E_{0r}}{E_{0i}} \right)_s = \frac{n_i \cos \theta_i - n_t \cos \theta_t}{n_i \cos \theta_i + n_t \cos \theta_t} = \text{Re} \left(|r_s| e^{i\delta_s} \right)$$

$$r_p = \left(\frac{E_{0r}}{E_{0i}} \right)_p = \frac{n_i \cos \theta_i - n_t \cos \theta_t}{n_i \cos \theta_i + n_t \cos \theta_t} = \text{Re} \left(|r_p| e^{i\delta_p} \right)$$

$$\rho = \frac{E_{pr}^{\text{refl}} / E_{ps}^{\text{incident}}}{E_{sr}^{\text{refl}} / E_{ss}^{\text{incident}}} = \frac{r_p}{r_s} = \frac{|r_p|}{|r_s|} e^{i(\delta_p - \delta_s)} = \tan(\Psi) e^{i\Delta}$$

Ψ and Δ are the "ellipsometric angles"

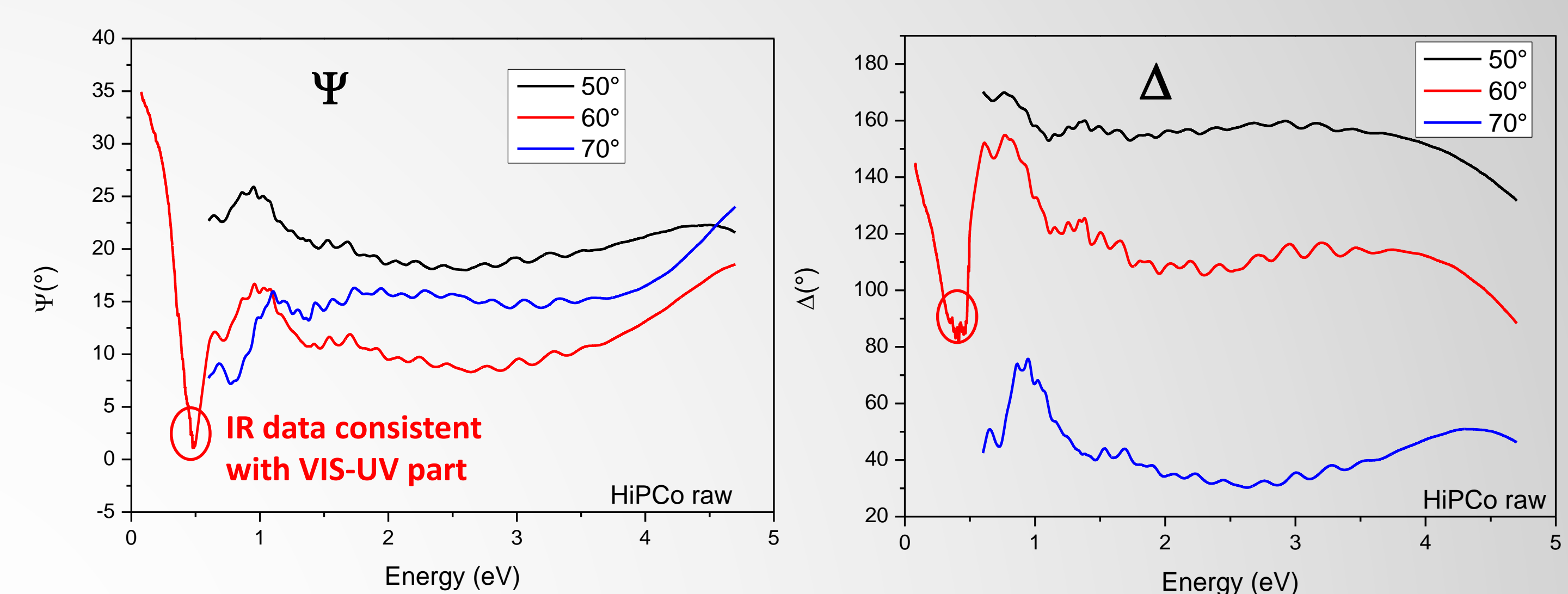
Raman spectroscopy



Few defects introduced by HNO₃ oxidation, many defects introduced by radical functionalization with MeOB groups.

(confirmed by XPS analysis, data not shown)

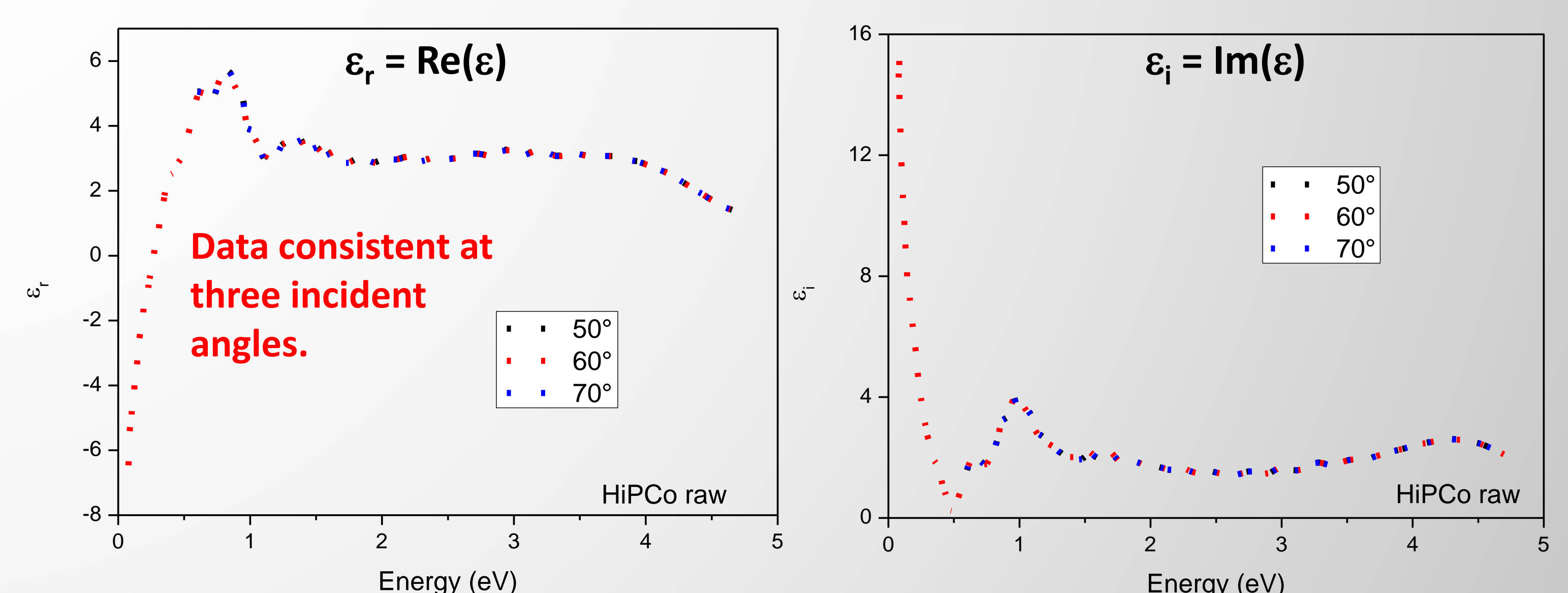
Data acquisition and analysis



SEMI-INFINITE, ISOTROPIC AND HOMOGENEOUS MEDIUM MODEL:

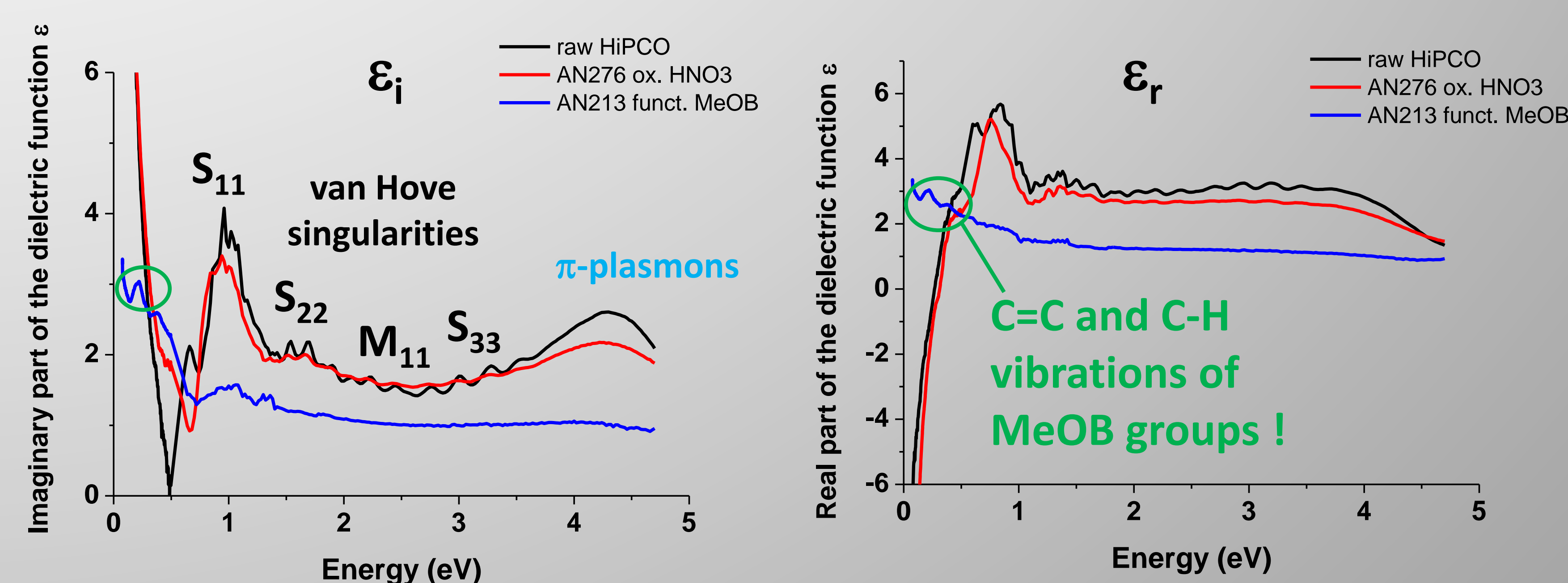
Analytical expression for the complex dielectric function :

$$\epsilon = \sin^2 \theta_i \left(1 + \left(\frac{1 - \tan \Psi e^{j\Delta}}{1 + \tan \Psi e^{j\Delta}} \right)^2 \tan^2 \theta_i \right)$$



VALIDATION OF THE MODEL

Dielectric functions of raw and modified SWCNTs ($\theta_i = 60^\circ$)



Functionalization strongly decreases the intensity of van Hove singularities and π -plasmon band (but not our microwave-assisted oxidation process).

Detection of MeOB functions !

Conclusion

Raman spectroscopy showed that ox-CNTs had almost the same D band intensity than raw CNTs, while MeOB-CNTs gave a quantitative increase of this band. The ellipsometric measurements showed very interesting complementary results. The dielectric function of the films was found independent on the incident angle, confirming *a posteriori* the hypothesis of a homogeneous and isotropic medium. Raw and ox-CNTs showed a negative ϵ_r function in the infrared spectrum, which corresponds to a metallic behaviour due to holes as charge carriers. This metallic behaviour was lost with MeOB-CNTs. This can be explained by a partial electron transfer from grafted groups towards CNTs, leading to a decrease of the number of holes and an increase of the CNT Fermi level. The covalent grafting also decreased intensity of the π -plasmon band at 4.5 eV and the peaks due to van Hove singularities. These conclusions agree with and go beyond those obtained from Raman spectroscopy. Our results exemplify the fact that spectroscopic ellipsometry is a powerful method to obtain precious information on the electronic effects resulting from the covalent functionalization of SWCNTs.