STUDYING THE CATALYTIC GROWTH OF SINGLE-WALLED CARBON NANOTUBES WITH IN SITU RAMAN MEASUREMENTS

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Catalytic chemical vapor deposition (CCVD) is a major method for the synthesis of carbon nanotubes (CNTs) and nanowires. Despite considerable progress in the control of the carbon nanotube length, orientation and structure, the fundamental processes involved in the nanotube nucleation, growth and termination still remain poorly understood. Rationalization is made difficult because CCVD combines the difficulties of different fields (heterogeneous catalysis, crystal growth, thin film deposition). The complexity of the problem especially arises when one considers the different chemical and physical processes involved, operating both on surface and in gas-phase, intricate at different time and spatial scales (molecular, nano, macro). Developing realistic growth models clearly requires the combination of theoretical and simulation works with reliable *in situ* data.

We chose to investigate the growth of SWNT using *in situ* Raman measurements because SWNT provide an intense, specific and structure-dependent Raman signature. We initiated a systematic study of the growth conditions for different catalyst-precursor couples. From our observations, at least two conditions are required for nucleating SWNT: the catalyst metal particle must be in a reduced state and they must reach a critical carbon concentration. Once reduced, catalyst particles quickly restructure, most noticeably at high temperatures. Being in kinetic competition with SWNT growth, catalyst restructuring reduces the lifetime and the yield of SWNT growth and shifts the SWNT distribution toward larger diameters.

In addition to SWNT, we evidenced the by-formation of disordered carbon nanostructures (DCN) by Raman and HRTEM. Their relative proportion is dependent on the kinetic equilibrium between the supply of carbon atoms from the gas precursor and their rearrangement at the surface of the catalyst particle. These processes also influence the kinetics of SWNT growth and its deactivation due to catalyst encapsulation by DCN. By studying the defect-induced D band of each structure (SWNT and DCN) as a function of the growth temperature, activation energies for the healing of defects can be extracted (figure 1).

Radial Breathing Modes (RBM) can also be exploited to monitor the distribution of SWNT diameter. In addition to the catalyst preparation, we observed that the growth conditions (temperature and precursor pressure) significantly influence the diameter distribution (figure 2). Most noticeably, the growth of small diameter nanotubes is promoted in a narrow domain of the parameters of growth. *In situ* Raman experiments were performed to identify the processes influencing the diameter distribution.

References

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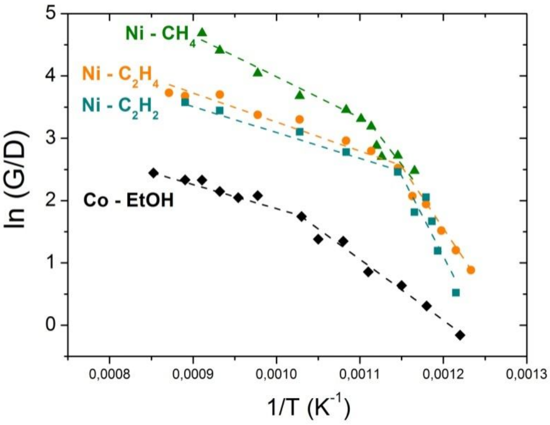

Figure1: Arrhenius plots of G/D as a function of the synthesis temperature

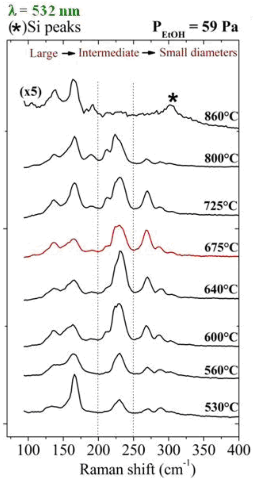

Figure 2: Evolution of the RBM profile as a function of the synthesis temperature

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