

Thursday, July 1

SESSION CHAIR: **ESKO KAUPPINEN**, *Aalto University***8:30-9:10 Keynote 4****How does a single-walled carbon nanotube grow from a nanoparticle? The role of the catalyst in nanotube growth**  
**Yoshikazu Homma**, *Tokyo University Of Science, Japan*

Carbon nanotube and graphene are two of the materials attracting much attention currently. A single-walled carbon nanotube (SWNT) has a shape of rolled-up graphene, but growth process is quite different from that of graphene. While a large graphene sheet grows horizontally on a flat surface, a SWNT grows vertically on a curved surface of a nanoparticle. Transition metals can form either graphene or nanotube depending on the curvature. Interestingly, SWNTs are rather easy to grow if nanoparticles present, as if the chemical nature of the nanoparticle is unimportant: silicon, silicon carbide, alumina, and diamond as well as various metals including gold, silver, and copper act as the catalyst of SWNT growth. The physical shape, i.e., the curved surface with a high curvature might be necessary to form a cap structure with carbon pentagons, which would act as a nucleus of SWNT. Furthermore, the phase of the nanoparticle, either liquid or solid, may not be crucial. Still, the catalyst seems to have another role: supplying carbon atoms to the nanotube. Without catalyst particles, SWNTs rarely extend. This is also true for the growth of graphene edges. On the particle surface, carbon bearing molecules might be converted to carbon atoms or other forms which can be incorporated into the edge of carbon hexagon networks. Recent progresses in SWNT growth would lead to better understanding of nanotube growth mechanism soon. Of great concern is the possibility of epitaxial growth of SWNTs from crystalline catalyst particles for chiral control of SWNTs.

**9:10-9:27 Contributed Talk 21****Catalytic Growth of Carbon Nanotube: Is the Size of Catalyst Determines the Diameter of Carbon Nanotube?**

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Single-walled carbon nanotubes (SWNTs) have attracted great deal of interests since their discovery. A SWNT can either be a semiconductor or metal, depend on its diameter and chiral angle. Furthermore, for those semiconducting ones, the band gaps are inversely proportional to their diameters. Therefore, the controlled synthesis of SWNTs with uniform diameters and chiral angles are critical for many practical applications. Abundant studies have suggested that the diameters of SWNTs were determined by the sizes of catalyst nanoparticles (NPs). However, the growth of small SWNTs from large catalyst NPs was also frequently observed. The diameter-controlled synthesis of SWNTs can only be fulfilled ground on unveiling the factors which can affect the diameters of SWNTs and know how they work. In this contribution, we employed high-resolution TEM transmission electron microscopy (HRTEM) and resonant Raman spectroscopy to study the catalyst size-SWNT diameter relationship in two chemical vapor deposition (CVD) processes, namely, supported catalyst and floating catalyst CVD processes. It is found that in a supported catalyst process, the as-grown SWNTs possess comparable diameters with the sizes of the Fe catalyst NPs; while the SWNT diameters constantly smaller than the catalyst sizes in floating catalyst process. An universal catalyst size-SWNT diameter relationship, which is suggested to be dependent

on whether the catalyst is homogeneous or heterogeneous (both in chemical composition and in structural), is proposed based on our experiment results and that of others. These findings have potential to guide the diameter controlled synthesis of SWNTs.

**9:27-9:44 Contributed Talk 22****Gas-phase and On-surface Decomposition of Ethanol in Alcohol CVD**

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We have previously investigated gas-phase thermal decomposition of ethanol and its effects on single-walled carbon nanotube (SWNT) synthesis by the alcohol catalytic CVD (ACCVD) method, and found that a significant fraction of ethanol quickly decomposes into various reactive byproducts such as C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, and CH<sub>2</sub>. Calculations using the CHEMKIN software package were in good agreement with FT-IR measurements of chemical species detected in the gas ambient. However, the relative contribution of these species to SWNT growth remains unclear. To resolve this issue, we extended our analysis using isotopically modified ethanol, in which one of the carbons was <sup>12</sup>C and the other <sup>13</sup>C. Since ethanol is asymmetric the carbons are expected to contribute unequally to SWNT formation. After thermally decomposing into symmetric byproducts such as C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>2</sub>, the <sup>12</sup>C and <sup>13</sup>C contribution should be equal. The degree of contribution was determined from the isotope-induced shift in the Raman G-band frequency. We find the inequivalent contribution from ethanol varies with CVD parameters, and is more exaggerated at minimal decomposition conditions, e.g. low temperature and/or high flow rate. One unexpected finding, however, is that our data indicate that ethanol decomposition is also promoted by the presence of Mo on the substrate. This indicates that the role of Mo in ACCVD is not only to immobilize the Co catalyst, but also to promote local ethanol decomposition at the substrate surface. A model quantifying the gas-phase and surface decomposition processes will be proposed, and the effects on SWNT quality will be discussed.

**9:44-10:01 Contributed Talk 23****Single-walled carbon nanotube nucleation, growth and termination studied by in situ Raman measurements**

**Vincent Jourdain**, *Université De Montpellier, France* | **Matthieu Picher**, *Université De Montpellier, France* | **Eric Anglaret**, *Université De Montpellier, France* | **Raul Arenal**, *LEM ONERA-CNRS, Châtillon, France*

Despite considerable progress in the control of the carbon nanotube length, orientation and structure, the fundamental processes involved in nanotube nucleation, growth and termination remain poorly understood. The complexity of the problem especially arises when one considers the different chemical and physical processes operating on surface and in gas phase, at different time and spatial scales. Develop realistic growth models clearly requires the combination of theoretical and simulation works with reliable in situ data. As other groups [1-2], we chose to investigate the SWCNT growth using in situ Raman measurements because SWCNTs provide intense and specific Raman spectra. We initiated a systematic study as a function of the growth conditions [3] and catalyst-precursor couples. From our observations, two conditions are required for the nanotube nucleation: the catalyst particle must be reduced and reach a critical carbon concentration. Once reduced, the catalyst particles rearrange quickly. The growth kinetics is generally limited by the carbon supply at the catalyst surface. The nanotube crystalline quality appears controlled by the kinetic equilibrium between the supply of carbon atoms and their surface diffusion/rearrangement. We observed two types of termination: a process dominant at high temperature and low carbon supply compatible with an Ostwald ripening of the particles and a process dominant at low temperature and high carbon supply compatible with a catalyst encapsulation by a carbon layer. 1. Kaminska et al.,