TEM study of Co-Ni nanoparticles catalysts extracted from laser-produced single-wall carbon nanotubes.

Nadi Braidy[1*], Zygmunt Jakubek[2], Benoit Simard[2] and Gianluigi A. Botton[1]

[1]Material Science and Engineering, McMaster University.
1280 Main Street West (Hamilton, ON), L8S 4L7, Canada.
[2]National Research Council of Canada. 100 Sussex Drive, (Ottawa, ON), K1A 0R6, Canada.
*E-mail: nadib@mcmaster.ca

The growth of single-wall carbon nanotubes (SWNTs) by the laser-oven method occurs in a chaotic environment composed of laser-vaporized C, Co and Ni species at elevated temperature (~1200 ºC) and at near-atmospheric pressure (500 Torr Ar). While several hypotheses have been put forward [1] to explain the growth mechanism, the exact role of the Co and Ni in the catalytic process is still subject to controversy and intense debate. An exhaustive analytical investigation of the Co-Ni NPs would provide an insight to fully address the complex problem of the growth mechanism and understand the dependency of the NPs composition on the catalysis of SWNTs. The purpose of this abstract is to present a summary of an quantitative electron energy-loss spectroscopy (EELS) investigation on Co-Ni alloyed NPs coproduced with SWNTs by the laser-oven method [2].

Co-Ni NPs were magnetically extracted from a sample of a solution of high-purity SWNTs produced with an improved version [3] of the dual laser-oven method [2]. A drop of the solution was left to dry on a holey amorphous carbon film supported on a copper TEM grid. The nanoparticles were analyzed using a JEOL 2010F electron microscope operated at 200 kV equipped with a Gatan Tridiem imaging filter. A high-purity Co-Ni thin standard of known composition was used to determine the k-factor suitable for quantitative EELS analysis of the Co-Ni NPs.

An overview of the sample (Fig. 1) shows large catalysts NPs with size varying from ~10 to 30 nm dispersed amongst bundles of SWNTs. The observation of the same sample in annular dark-field scanning-TEM (Fig. 3, insert) also reveals the presence of numerous clusters and smaller NPs. While the larger NPs (>~5 nm) mostly appear to be encapsulated by a set of graphene layers (Fig. 2), the smaller NPs (<~5 nm) appear free from graphene wrapping.

Quantification at the 95% confidence level of the raw EELS spectrum obtained from the ~2.2 nm NP (Fig. 3, insert: indicated by the arrow) yields a Co:Ni ratio of ~1.7 ± 0.5 (62 ± 5 % Co). In a similar way, we have analyzed the composition of 60 Co-Ni NPs as a function of their size (Fig. 4). While the small NPs (<5 nm in diameter) show a marked Co enrichment, the Co content of the large NPs (>5 nm) appear to be somewhat smaller than that of the target (Co:Ni 1:1).

This quantitative procedure was also applied to the data of a linescan acquired across two ~10 nm Co-Ni NPs (Fig. 5). The error analysis of each of the spectrum composing the linescan was computed and is displayed along with the absolute intensity of the Co and Ni edge. The data indicates small, but statistically significant variation of the composition across the NPs.

This study presents the first systematic analysis revealing the composition distribution of the SWNTs catalysts. Our results therefore present significant findings that need to be considered in models describing the growth mechanism of SWNTs. Further work will focus on the origin of the apparent Co enrichment of smaller NPs and the exact nature of the nanocrystalline phase of the smaller NPs since non-equilibrium phenomena and size effects play a significant role on the phase stability and consequently, on the catalystic properties of NPs.

Acknowledgments:
The authors acknowledge C. Kingston for the sample, J. Garret for the standard preparation and A. Duft and F. Pearson for microscopy assistance. We also thank CFI, NRC and NSERC for funding of the infrastructure and the research activities.

References:
[1] A. Moisala *et al*, J. Phys: Cond. Matt., **15** (2003) S3011.
[2] A. Thess *et al.*, Science, **273** (1996) 5274.
[3] C. Kingston and B. Simard. Carbon, (2004) In press.

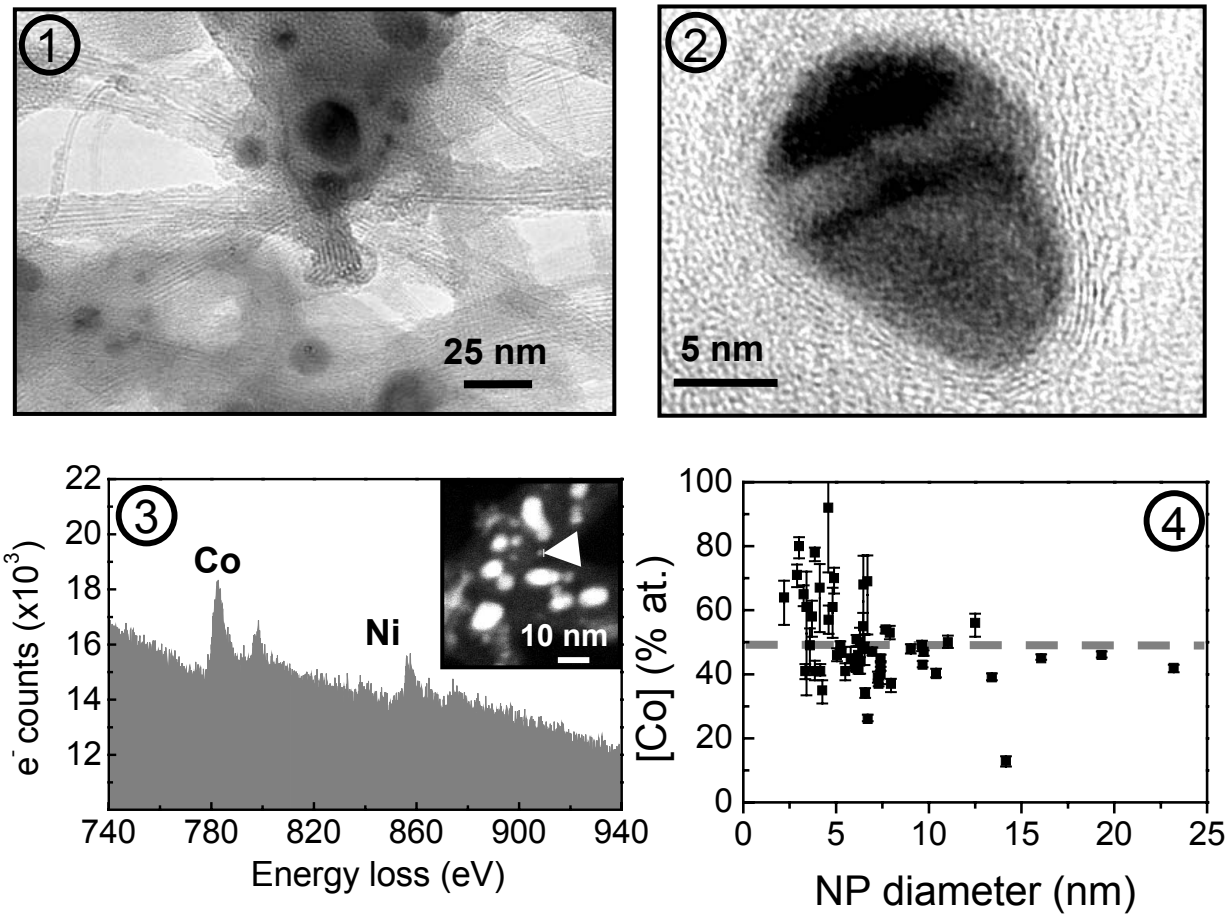

Fig. 1. Overview of the magnetically extracted sample of the laser-produced SWNTs. **Fig. 2.** HREM of graphene-encapsulated Co-Ni nanoparticles. **Fig. 3.** Electron energy loss spectrum of NP indicated by an arrow in the high-angle annular dark-field scanning TEM image displayed in insert. **Fig. 4.** Composition of 60 Co-Ni NPs as a function of their size. **Fig. 5.** EELS linescan across the center of two NPs: Co content (squares) along with the absolute intensity of the Co (triangles) and Ni (circles) extracted edges for each spectrum recorded along the line.