Radicals-assisted CVD implemented in a modified HR environmental TEM for in-situ real-time SWCNTs growth with a given chirality

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Materials science of carbon nanotubes (CNT) lies at the intersection of various paradigms from fundamental to applied physics and chemistry. Recognizing how the different concepts can be combined together to understand CNT formation still remains a challenge. The synthesis of CNTs with desired chirality and diameter is one of the most important challenges for the nanotubes science and achieving such selectivity requires a good understanding of their growth mechanism. There is an overwhelming body of evidence that catalytic growth is the most promising method for the CNTs synthesis, especially for reaching a chiral selectivity synthesis.[1,2] Although knowledge of the different stages of growth has advanced considerably[3] a full picture is still elusive. Mastering chirality control, however, requires a deeper understanding of the very early stage of CNT nucleation, when the symmetry type is set. A well-controlled synthesis of catalyst nanoparticles (composition, morphology, size) appears to be a mandatory condition for controlling the characteristics of the as-synthesized nanotubes.[4] Recent researches focused especially on the growth of multiwalled CNT[5,6] have shown that the catalyst (re)shaping is correlated with surface energy modification due to C adsorption. To the best of our knowledge previous works have been devoted to the understanding of the relationship between changes in catalyst particle morphology and CNT nucleation [7-11] but more quantitative description is greatly needed for the elaboration of SWCNTs with defined chirality.

The aim of the present study is to complement the well-established ex-situ observation of SWCNTs growth [12, 13] with real-time, in-situ TEM observations of the real CVD growth reactions without losing significant resolution. The study presents the development of a unique approach that combines the HRTEM technique, with the implementation of radical-assisted CVD gas sources in a modified environmental transmission electron microscope (ETEM) equipped with a Cs image aberration-corrector. The new set-up, well adapted for carrying out real-time in-situ observations, allows one to keep a higher vacuum within the TEM chamber while bringing gas molecules to the sample, was used to analyze catalyst reshaping and its morphology dynamics during CNT nucleation/growth under controlled conditions. As applied to different new and controlled bimetallic nanoalloy catalysts types, such as CoRu, FeRu and NiRu catalyst [11], the emphasis is to understand the role played by the catalyst and put forward a growth mechanism essential to realized SWCNTs with specific and targeted chirality. In particular, we will discuss the role of the growth temperature and the chemical composition of the catalyst on the final SWCNTs structure.

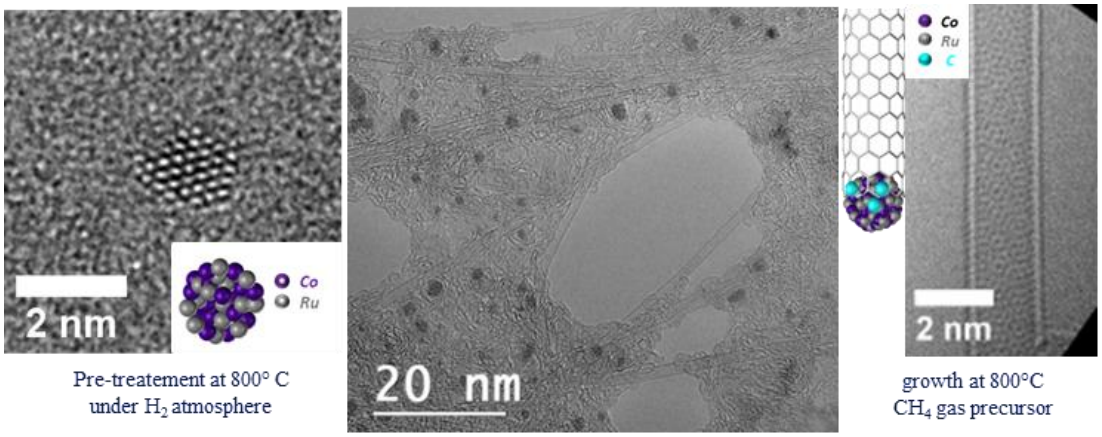

Figure 1: Ex-situ HRTEM observations of CoRu bimetallic catalyst treated at 800°C under H_2 atmosphere (left); corresponding SWCNTs which are grown using CH_4 as gas precursor(middle); HRTEM image of an SWCNT (right).

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References:

[1] Hersam, M. C.- Nat. Nanotechnol. 2008, 3, 387 - 394.

[2] Harutyunyan, A. R.; Chen, G.; Paronyan, T. M.; Pigos, E. M.;Kuznetsov, O. A.; Hewaparakrama, K.; Kim, S. M.; Zakharov,D.; Stach, E. A.; Sumanasekera, G. U. - Science 2009, 326, 116 - 120

[3] Ding, F.; Harutyunyan, A. R.; Yakobson, B. I. - Proc. Natl. Acad. Sci. U.S.A. 2009, 106, 2506 - 2509

[4] H. Dai, A. G. Rinzler, P. Nikolaev, A. Thess, D. T. Colbert, R. E. Smalley, Chem. Phys. Lett. 260, 471-475, (1996)

[5] Rodriguez-Manzo, J. A.; Terrones, M.; Terrones, H.; Kroto, H. W.; Sun, L.; Banhart, F.. Nat. Nanotechnol. 2007, 2, 307 - 311.

[6] Yoshida, H.; Takeda, S.; Uchiyama, T.; Kohno, H.; Homma, Y. Nano Lett. 2008, 8, 2082 - 2086.

[7] Hofmann, S.; Sharma, R.; Ducati, C.; Du, G.; Mattevi, C.; Cepek, C.; Cantoro, M.; Pisana, S.; Parvez, A.; Cervantes- Sodi, F.; et al.. Nano Lett. 2007, 7, 602 - 608.

[8] Sharma, R.. J. Mater. Res. 2005, 20, 1695 - 1707

[9] He, M., Fedotov, P.V., Chernov, A., Obraztsova, E.D., Jiang, H., Wei, N., Cui, H., Sainio, J., Zhang, W., Jin, H., Karppinen, M., Kauppinen, E.I., and Loiseau, A., , Carbon 108, 521-528 (2016).

[10] Picher M., Lin P. A., Gomez-Ballesteros J. L., Balbuena P. B. and Sharma R., Nano Lett.14, 6104 (2014).

[11] Lin M., Tan J. P. Y., Boothroyd C., Loh K. P., Tok E. S. and Foo Y. L., Nano Lett. 6, 449 (2006

[12] Castan A., Forel S., Catala L., Florea I., Fossard F., Bouanis F., Andrieux-Ledier A., Mazerat S., Mallah T., Huc V., Loiseau A., Cojocaru C.-S.- Carbon 123 (2017) 583-592.

[13] Bouanis F. Z., Florea I., Bouanis M., Muller D., Nyassi A., Le Normand F., Pribat D. - Chemical Engineering Journal 332 (2018) 92 - 101.