SWNT GROWTH MODES AND CHIRAL SELECTIVITY STUDIED BY COMPUTER SIMULATION

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Introduction

Single wall carbon nanotubes (SWCNTs) observed by Ijima in 1991 present metallic or semiconducting properties depending on their chirality. SWCNTs are usually synthesized by catalyst chemical vapor deposition (CCVD). This technique consists in acting a carbon precursor on a metallic nanoparticle catalyst (NP), in order to catalyze carbon atoms and initiate tube growth. Experimentally, nanotubes grown by CCVD present a large dispersion in length, diameter and chirality. Structural selectiveness is actually blocking nanotube devices dissemination. Structural and chiral selectivity represent a challenge which focuses efforts since 25 years, without the problem was solved so far. We show that diameter and length of nanotubes can be directly control by the carbon concentration dissolved inside the catalyst during the growth. We then report a key parameter explaining some experimental results that could allow in-situ chiral control of SWCNT in CCVD.

Materials and Methods

On the basis of a fourth moment tight binding Monte Carlo model developed for Ni-C materials[1], we simulate wetting properties of a catalyst in function of the carbon content dissolved inside the nanoparticle (x_c). We developed a thermodynamical model parametrized from DFT calculations in order to account different chemical properties of transition metal catalysts interacting with SWCNT.

Results and Discussion

We evidence different SWCNT growth modes so-called "tangential" and "perpendicular", depending on the carbon concecntration inside the catalyst, (figure 1.a). This behavior can be generalized for various nanoparticle (NP)/tube diameter ratios. At low x_c, far from the limit of solubility, catalyst wets the inner part of the CNT. This low concentration behavior ensure an energy minimization by healing the surface of the NP with CNT wall (figure 1.b). In turn, outer volume of the particle decreases and reach the limit of solubility with the remaining dissolved carbon atoms. In tangential growth mode, NP favors encapsulation by the SWCNT. In other words, a prematurated stop of the growth corresponding a short SWCNT length. Note that in tangential mode, tube diameter is mostly determined by the initial NP diameter and growth T. On the other hand, perpendicular growth mode, corresponding larger x_c (figure 1.a), gives finner and longer nanotubes. These behaviors has been verified experimentally[2,3]. About chirality, we

identify a key parameter as edge energy of the tube interacting with the catalyst. Indeed, two sites can be distinguish from the tube edge : zigzag and armchair C sites. Detailing carefully energetic of SWCNTs on NPs, we plot SWCNT chiral diagrams which give stable chirality as a function of 2 C edge sites energetics, (figure 1.b,c). We show that chirality depends on thermal entropy, strength of metal carbon interactions between tube edge/catalyst and chemical nature of the catalyst.
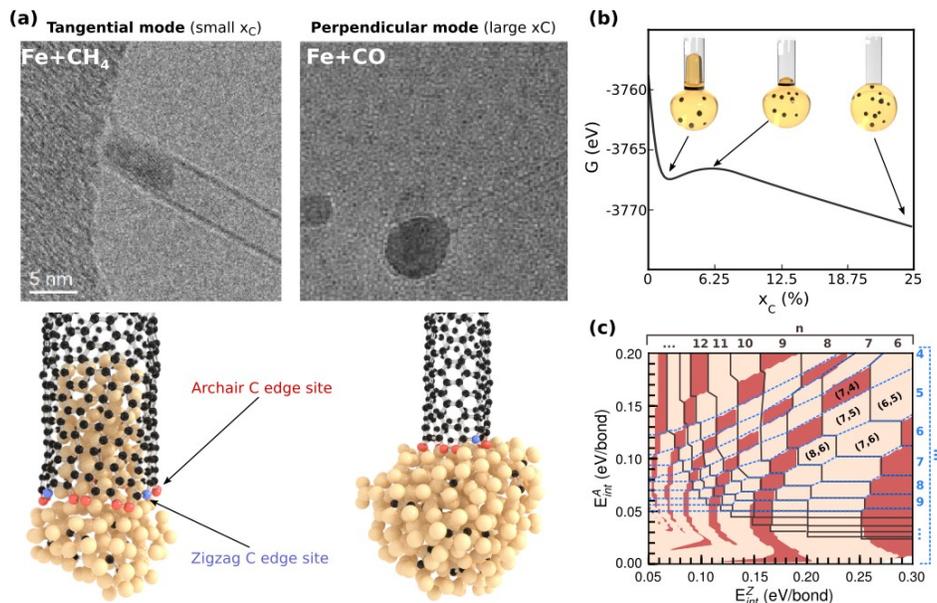

Figure 1. a) TEM images and simulated tangential and perpendicular growth modes depending on carbon concentration inside the catalyst. b) Free energy depending on carbon concentration. Chirality diagram depending on contact energy between zigzag and armchair C edge sites with a Ni catalyst. Brown area denotes metallic (n,m) tubes chirality, ligth grey denotes semiconducting (n,m) tubes chirality.

Conclusions

We emphasize the key role played by carbon solubility in the catalyst during SWNT synthesis. We show that length and diameter of SWCNT can be controled by the carbon concentration in the catalyst. Based on DFT data and a thermodynamical model, we discuss a possible way to control SWCNT chirality during the synthesis by tunning chemical properties of the catalyst.

Acknowledgment

References

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