High Purity Synthesis of (6,4) Single-Walled Carbon Nanotube by Surface State Control of Co Catalyst

Bin Xu[1], Toshiro Kaneko[1], Yasushi Shibuta[2], Toshiaki Kato[1]

[1] Department of Electronic Engineering, Tohoku University, [2] Department of Materials Engineering, University of Tokyo
E-mail: xu12@ecei.tohoku.ac.jp

1. Introduction

Single-walled carbon nanotubes (SWNTs) have many outstanding properties due to the unique 1-dimensional structure. Especially, fabrication of the high performance device utilizing the intriguing opt-electronic property is regarded as a very promising output. However, the opt-electronic property is decided by the helicity of graphene wrapping, which is defined as SWNTs chirality, making the chirality control of SWNTs a very critical issue. Towards this goal, many researches about the precise control of catalyst are reported and the effects of catalyst size [1] and crystal structure [2] are well studied. On the other hand, the correlation between catalyst surface condition and chirality is seldom being studied, and the details still remain unclear. In this study, systematic investigations are carried out aiming for the elucidation of the correlation between SWNTs chirality and catalyst surface condition.

2. Experiment

Synthesis of SWNTs is carried out using a home-made diffusion type plasma CVD apparatus [3]. As for the surface condition control of catalyst, a new method is developed. In this method, oxidation degree of catalyst surface can be well controlled by ultra-high vacuum annealing. The small amount of reactive gas species are added during the annealing process, which can precisely tune the surface state of catalyst. The catalyst surface condition is evaluated using energy dispersive X-ray spectrometry (EDX), X-ray photoelectron spectroscopy (XPS), X-ray absorption fine structure (XAFS), and extended X-ray absorption fine structure (EXAFS). The chirality distribution of SWNTs is measured by photoluminescence-excitation (PLE) mapping and ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectroscopy.

Through the adjustment of the catalyst pretreatment condition (Fig. 1(a)), a significant shift in chirality can be obtained from (6,5) to (6,4) predominated (Fig. 1(b)-(e)). To find out the correlation between catalyst surface condition and SWNTs chirality, detailed comparison between theoretical model about SWNTs nucleation and experimental results are made. For this comparison, the biding energy of SWNTs and Co catalyst with different oxidation degree is calculated with a first principles calculation. Based on this calculation, lift-off energy for nanotube cap increases with an increase in catalyst surface reduction rate. The simple estimation using calculated binding energy and theoretical model shows that the most preferred chiral angel for SWNTs growth within this diameter range shift to a smaller chiral angel with the reduction of catalyst. These are in good accordance with the experimental results.

Further optimization of catalyst surface state based on the established chirality selective mechanism is carried out, resulting in the preferential growth of (6,4) SWNTs with very high purity 57% for the first time (Fig. 1(d)(e)).

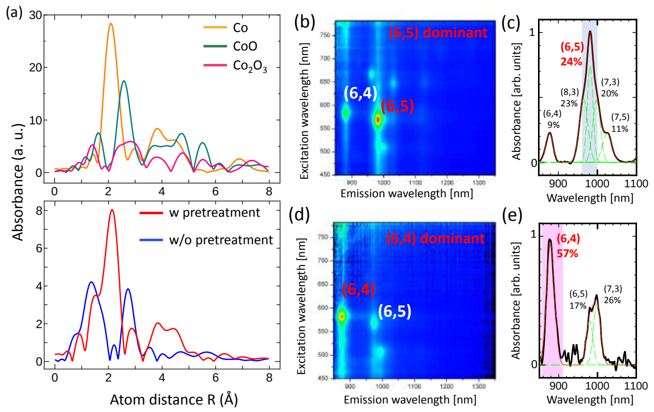

Fig. 1. (a) Typical XAFS spectra of Co catalyst (blue) before and (red) after the catalyst pretreatment. The upper part in (a) shows the control spectra with Co, CoO and Co_2O_3. (b)-(e) (b,d) PLE map and (c,e) UV-Vis-NIR spectra of SWNTs grown from catalyst (b,c) before and (d,e) after pretreatment.

3. Conclusions

The growth of high purity (6,4) SWNTs is realized by controlling the oxidation degree of Co catalyst. The theoretical calculation and first principle calculation show that the transition of dominant chirality from (6,5) to (6,4) SWNTs can be due to the different binding energy between SWNTs and oxidized Co catalyst. Our results indicating the catalyst surface condition control can be a promising way towards the ultimate goal of SWNTs growth with desired chirality.

References

[1] M. Picher, E. Anglaret, R. Arenal and V. Jourdain, ACS Nano **5** (2011) 2118.
[2] F. Yang, et al., Nature **510** (2014) 522.
[3] T. Kato and R. Hatakeyama, Nature Nanotechnology **7** (2012) 651.