

Chirality-Dependent Reactivity to O₂ of Single-Walled Carbon Nanotubes

Bilu Liu^{1,2}, Hua Jiang¹, Arkady Krasheninnikov³, Albert Nasibulin¹, Wencai Ren², Chang Liu², Hui-Ming Cheng², Esko I. Kauppinen^{1*}

¹ Nanomaterials Group, Department of Applied Physics and Center for New Materials, Aalto University School of Science, 00076 AALTO, Finland

² Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

³ Department of Physics, University of Helsinki, P.O. Box 43, 00014 University of Helsinki, Finland

1. Introduction

Single-walled carbon nanotubes (SWCNTs) are known by their unique electronic, optical, mechanical, and chemical properties and show great promise for applications in many fields including nanoelectronics. Electronic properties of SWCNTs depend critically on their chiral structure, thus, a precise control over nanotube chirality is desired for practical applications of SWCNTs. For this purpose, either selective growth [1] or post-growth separation [2] strategies have been developed, both of which are based on the reactivity dependence of SWCNTs on their structure. It is fundamentally important to understand the relationship between the atomic structure of the SWCNTs and their energetic and reactivity experimentally. Here, we developed a unique approach which allow assessing the chirality-dependent reactivity of SWCNTs.

2. Methods and results [3]

High quality SWCNTs were grown using floating catalyst chemical vapor deposition (CVD) method and they were directly collected onto a Si₃N₄ transmission electron microscopy (TEM) grid. Electron diffraction technique were employed to determine the chiralities of individual SWCNTs. With the aid of the indexed TEM grid, an investigated SWCNT can be conveniently tracked in TEM before and after oxygen treatments. Firstly, an individual SWCNT was found in the microscope and its location was recorded. Meanwhile, an electron diffraction pattern of the nanotube was taken for chirality determination. Then, the grid underwent air treatment at a certain temperature, say 400 °C, for 30 minutes before it was put back into the microscope again to examine whether the investigated nanotubes were reacted or not. Afterwards, the grid underwent a second round air treatment at higher temperature followed by the TEM inspection. After a series of air treatments, image recording, and structure characterization of a large number of individual SWCNTs, a chirality map illustrating the chirality-dependent reactivity of SWCNTs to O₂ can be built up, based on which the dependence of such reactivity on diameters, metallicity, and chiral angles of nanotubes were demonstrated.

the evolution of an individual SWCNT after being treated at different temperatures of 400 °C, 450 °C, 470 °C, and 490 °C. The original SWCNT before the air treatment is shown in Fig. 1a (indicated by a solid arrow). Fig. 1b shows a typical electron diffraction pattern which features a set of parallel diffracted layer lines in addition to the bright spot at the center. The diffraction pattern was indexed and the chiral indices of the SWCNT were determined to be (11,10). It is clearly seen that the SWCNT stayed after the O₂ treatments at 400 °C (Fig. 1c), 450 °C (Fig. 1d) and 470 °C (Fig. 1e) but disappeared at 490 °C (Fig. 1f). It is worth noting that we did not observe a significant change in the surrounding carbon nanotube network. Thus the disappearance of the nanotube at 490 °C can be attributed to its reaction to O₂. Using the similar method, we systematically investigated the reaction of over 80 individual SWCNTs, on base of which we constructed a chirality-dependent reaction sequence of SWCNTs.

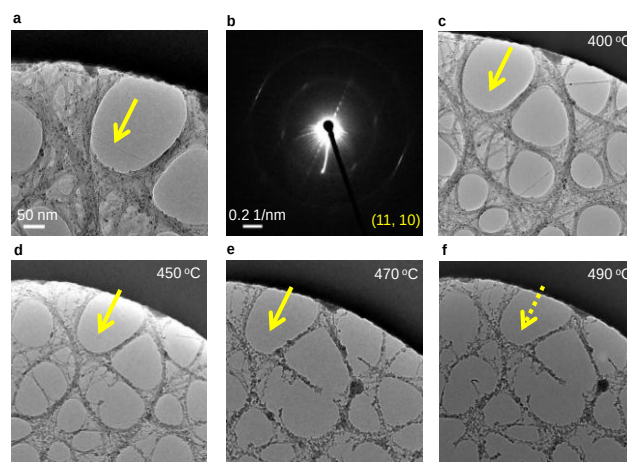


Fig. 1 The evolution of an individual SWCNT during the air treatment at different temperatures. (a) A TEM image of a pristine SWCNT; (b) the ED pattern of the SWCNT from which the chirality of the tube was determined as (11, 10). TEM images of the same nanotube after treatment for 30 min at 400 °C (c), 450 °C (d), 470 °C (e), and 490 °C (f). The solid arrows in image (a), (c), (d), and (e) indicate the nanotube, while the dotted arrow in image (f) indicates the disappearance of this nanotube.

Figure 1 presents a TEM image sequence illustrating

Figure 2a shows a chirality map of SWCNTs reacted at different temperatures, illustrating a clear trend of the reaction towards nanotubes with larger diameter and higher chiral angle as reaction temperatures increased from 400 °C to 490 °C (indicated by the red arrow). This trend is applicable to both semiconducting (Fig. 2b) and metallic SWCNTs (Fig. 2c). Those results suggest a preferential oxidation of small diameter SWCNTs apparently due to their high curvature nature. In addition, the metallic SWCNTs are subject to higher reactivity than their semiconducting counterparts of similar diameter and chiral angles due to their delocalized electronic states near the Fermi level. Furthermore, SWCNTs with higher chiral angles are less reactive and thermodynamically more stable as compared to those with small chiral angles of similar diameters and metallicity.

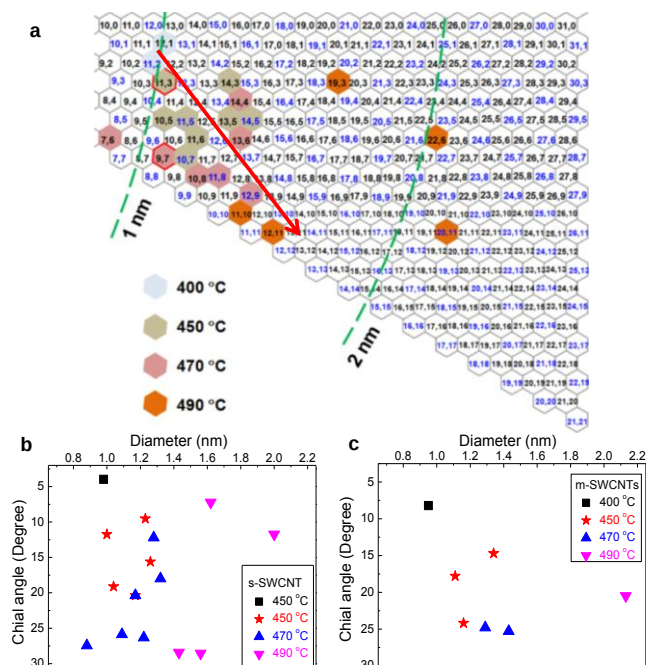


Fig. 2. (a) A chirality map of SWCNTs which reacted at different temperatures with a red arrow pointing toward large diameter and high-chiral-angle direction. Diameter and chiral-angle-dependent reactivity of (b) semiconducting, and (c) metallic SWCNTs.

3. Conclusions

In summary, selective chemical reactivity of single-walled carbon nanotubes (SWCNTs) in an O₂ atmosphere was demonstrated being chirality dependent. In general, SWCNTs with large diameters, high chiral angles, and of semiconducting properties are less reactive to O₂. The reactivity of the nanotubes decreases with increasing diameter; while for the same diameter, nanotubes with higher chiral angle are more stable than those with a small angle. Besides, metallic nanotubes appear energetically more in-

clined for O₂ absorption than semiconducting, thus they are less stable upon reaction with O₂. Our results demonstrate the dynamic interplay between electron structure and chemical reactivity of SWCNTs, therefore, imply an effective means to the modification of electronic structure of SWCNTs by chemical processes.

Acknowledgements

This work was supported by the CNB-E Project in Aalto University through the Multidisciplinary Institute of Digitalization and Energy (MIDE) program.

References

- [1] W. H. Chiang and R.M. Sankaran, *Nat. Mater.* **8** (2009) 882.
- [2] G. Y. Zhang et al., *Science* **314** (2006) 974.
- [5] B. L. Liu et al., in preparation (2012).