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Chirality distribution control of single-walled carbon nanotubes from nonmagnetic catalyst by diffusion plasma CVD

非磁性触媒利用拡散プラズマCVDによる
単層カーボンナノチューブの構造制御合成

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Single-walled carbon nanotubes (SWNTs) take on hollow cylinders formed by rolling up a graphene sheet made up of hexagonally bonded sp^2 carbon atoms. The direction and magnitude of a roll-up vector prescribe the chirality and diameter of the resulting tube, respectively. These geometric parameters in turn determine the tube's electronic band structure. However, making SWNTs of defined structures still remains to be a major challenge in the fundamental studies and applications of SWNTs. In this paper we show the first result on the narrow-chirality distributed SWNTs using a gold-catalyzed plasma chemical vapor deposition (PCVD) method through adjusting the H_2 gas and their electronic properties.

1. Introduction

One dimensional single-walled carbon nanotubes (SWNTs) are potential materials for future nanoelectronics [1]. Since the electronic and optical properties of SWNTs strongly depend on their diameter and chiral angle, the selective synthesis of SWNTs with desired chiralities is one of the major challenges in nanotube science and applications [2]. Some progress has been made by silica supported CoMo [3] and zeolite supported FeCo [4] catalysts. FeRu [5] and FeNi [6] catalysts have also been developed for the narrow chirality distribution. Noticeably, all of these results on the narrow chiraity distribution growth have been limited to the case of using magnetic catalysts. In spite of recent improvements in the SWNTs growth with nonmagnetic catalysts [7-8], the diameter and chirality (n,m) distribution control with the nonmagnetic catalysts is still highly required for the variety of applications.

2. Experimental

Figure 1 represents the schematic of experimental apparatus. The electrode distance (d_{ele}) is 10 mm and the anode-substrate distance (d_{sub}) is 50 mm. It is possible to generate plasmas under various pressures ranging from 50 Pa (low) to 10 kPa (high) in this system. On purpose to supply feedstock gases uniformly, mesh grids are used as the electrodes. Since

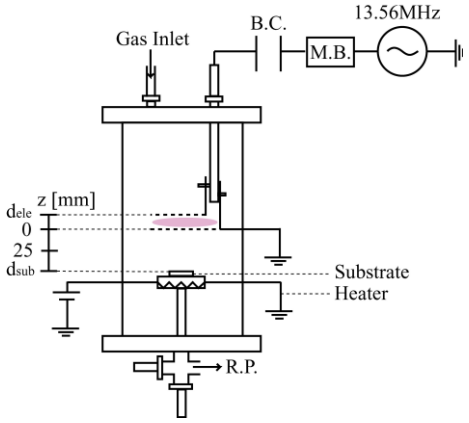

Fig. 1: Schematic of experimental apparatus.

growth process is carried out in a diffusion plasma region, the high quality SWNTs growth is considered to be realized.

The SWNTs production is performed on a substrate layered with Au, Al_2O_3, SiO_2, and Si. The gas pressure (P_g) is 60 Pa and the growth time (t) of SWNTs is 1 min.

3. Results and Discussion

Here we demonstrate a narrow-chirality distributed growth of SWNTs from an Au catalyst. The chirality and diameter distribution is analyzed by photoluminescence excitation/emission (PLE) spectroscopy, UV-vis-NIR absorption spectroscopy,

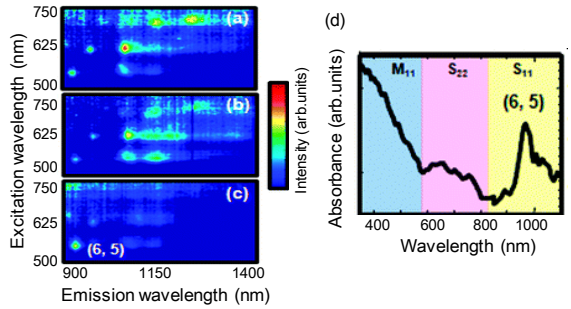

Fig. 2: PLE maps of SWNTs from Au catalyst by PCVD at (a) 0-sccm, (b) 3-sccm, and (c) 7-sccm H_2 flow rates, respectively. (d) UV-vis-NIR spectrum of SDS-dispersed SWNTs from Au catalyst at 7-sccm H_2 flow rate.

and Raman scattering spectroscopy with multi-lasers excitation. Based on the systematic investigation using the different combinations of catalyst types (magnetic or nonmagnetic) and chemical vapor deposition (CVD) methods (thermal CVD (TCVD) or plasma CVD (PCVD) [9]), PCVD with the nonmagnetic catalyst under an appropriate H_2 concentration is found to be critical. Figures 2 (a-c) and (d) show the PLE mapping and the UV-vis-NIR optical absorbance spectrum of the Au synthesized SWNTs by the PCVD method with (6,5) dominant SWNTs, respectively. We have for the first time demonstrated the selective growth of (6,5) rich SWNTs from the nonmagnetic catalyst [10].

This indicates hydrogen-assisted Au catalyzation is one of the critical factors to realize the narrow chirality distribution, which is in good agreement with theoretical predictions. The first-principle calculation by Yazyev *et al*. reveals that coinage metals such as Cu, Ag, and Au produce narrow chirality distributions [11]. Ding *et al*. report the SWNTs diameter is larger on the surface of Fe, Co, and Ni particles than Cu, Pd, and Au particles because of the different bond energies on the catalyst surface [12]. Following these theoretical models, we can explain the effect of H_2-assisted Au catalyzation on the narrow chirality distirbution as follows. Since the binding energy of hydrocarbons on the Au surface is much weaker than that on the Fe surface, it is difficult in the large-diameter case of Au catalyst to achieve the cap formation [12]. Additonal H_2 also enhances the etching of carbon precursor from the catalyst surface, which strongly suppresses the growth of large diameter SWNTs, and hence the chirality distribution grown from the Au catalyst can be narrower than that from the Fe catalyst. The stability of the cap structure migh be a possible reason why the (6,5) tube is dominant in this small diameter Au-PCVD SWNTs. The number of cap structures, which satisfy the isolated pentagon rule, is highly limited for small diameter SWNTs, and (6,5) is known to have one of the stable cap structures in this diameter range.

4. Conclusion

In conclusion, we have for the first time demonstrated the narrow-chirality distributed growth of SWNTs from the nonmagnetic catalyst. The Au catalzed PCVD growth under the appropriate hydrogen concentration is figured to be the critical factor in achieving the narrow chirality distribution. This narrow-chirality distributed SWNTs selectively grown from the nonmagnetic catalyst could be attractive to both fundamental studies of intrinsic magnetic properties of SWNTs and industrial applications to nanoelectronics.

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