

## Proof-of-Principle Plasma Processing on the Growth of Single-Walled Carbon Nanotubes Originating from a Single Carbon-Nanoring

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Since physical and chemical properties of single-walled carbon nanotubes (SWNTs) are determined by their sidewall structure (chirality), the chirality-selective growth of SWNTs has been a long-standing challenge toward their practical applications such as electronics, where strategies for its realization have mainly been based on using various kinds of metal catalysts [1]. Here, it is found for the first time that plasma-enhanced chemical vapor deposition (PECVD) enables the precisely structure(chirality)-controlled SWNT to grow from a single hoop of carbon six-membered rings (carbon nanoring: CNR) [2] without using any metal catalyst regarded as an impurity.

Our experiments are performed using a PECVD system consisting of an RF-discharge quartz tube and an electric furnace surrounding its center neighborhood, where the RF power is 150 W. Generated plasmas of electron density  $n_e$  and temperature  $T_e$  are provided to a SWNT-growth substrate of temperature  $T_{sub}$  placed within the furnace site. Here the plasmas are classified into “mild” ( $n_e \sim 10^8 \text{ cm}^{-3}$ ,  $T_e \sim 0.3 \text{ eV}$ ) and “harsh” ( $n_e \sim 10^9 \text{ cm}^{-3}$ ,  $T_e \sim 2.0 \text{ eV}$ ) plasmas in accordance with the intensity of plasma flux to the substrate. In addition, the thermal CVD (TCVD) process can also be carried out by switching off the RF power to compare with PECVD.

The chemical name of CNR as the seeded-growth molecule is  $[n]$  cycloparaphenylenes ( $[n]$ CPPs) that can be viewed as simple units of  $(n,n)$  armchair SWNTs with metallic property, where  $n$  denotes the number of benzene rings in the nanohoop (Fig. 1(a)). In our experiments  $n$  ranges from 6 to 12 corresponding to the diameters of 0.8 nm to 1.7 nm, each of which is spin-coated on a C-plane sapphire substrate in the form of solvent (toluene) solution of CPPs. Concerning the CVD process,  $\text{C}_2\text{H}_5\text{OH}$  is used as the feed carbon source,  $1.3 \times (10 \sim 10^3) \text{ Pa}$ , and most attention is given to the conditions of nanocarbon-growth substrate, i.e., growth temperature ( $T_{sub}$ ) and difference of plasma-influx intensity (mild, harsh) in the ethanol plasma. On SWNT-characterization technique, Raman scattering spectroscopy is mainly adopted, which provides an invaluable analytical tool for identifying molecules and estimating the crystalline quality. In the following paragraph we mainly describe experimental results for the CVD time of 15min and very low  $T_{sub}$ .

**(1)  $T_{sub}=350 \text{ }^\circ\text{C}$  and mild-plasma influx :** As might be expected, no change in molecule morphology on the substrate surface occurs at this low temperature in the case of TCVD. A weak Raman-spectrum peak in the low-frequency range of  $100\text{-}300 \text{ cm}^{-1}$ , on the contrary, is

observed in any of the PECVD cases adopting  $[n]$ CPP ( $n=6\sim 12$ ). This Raman peak is called as the radial breathing mode (RBM) coming from vibrations of the atoms in the radial direction of the tube, which is used to identify the SWNT species. According to a relationship between SWNT diameter ( $d$ ) and RBM frequency, the estimated  $d$  is close to any diameter of the adopted  $[6]\sim[12]$ CPPs. Furthermore, the PECVD performance for  $[10]$  and  $[12]$  CPPs exhibits a striking change in Raman spectra, as typically presented in Figs. 1 (b) and (c) for  $[12]$ CPP, where a peak much stronger than G(graphite)-band ( $1592 \text{ cm}^{-1}$ ) and D(defect)-band ( $1300 \text{ cm}^{-1}$ ) peaks appears at  $159 \text{ cm}^{-1}$  in the low-frequency range. In addition, the spectrum line shape in the G-band range includes a clear peak of the lower-frequency component at  $1546 \text{ cm}^{-1}$  in addition to  $G^+$  and  $G^-$ , which is called as BWF component characterizing metallic/armchair SWNTs. Thus, the (12,12) SWNT is verified to grow from the  $[12]$ CPP at very low temperature of  $350 \text{ }^\circ\text{C}$ . This is the first long-heralded result as the precisely structure(chirality)-controlled growth of SWNTs from the CNR since CPPs were synthesized by organic chemists.

**(2)  $T_{sub}=350 \text{ }^\circ\text{C}$  and harsh-plasma influx :** The G-band and D-band intensities in Raman spectra becomes much weaker and stronger, respectively, compared with the mild-plasma case. Namely, SWNTs are deformed during their growing phase due to a stronger plasma etching.

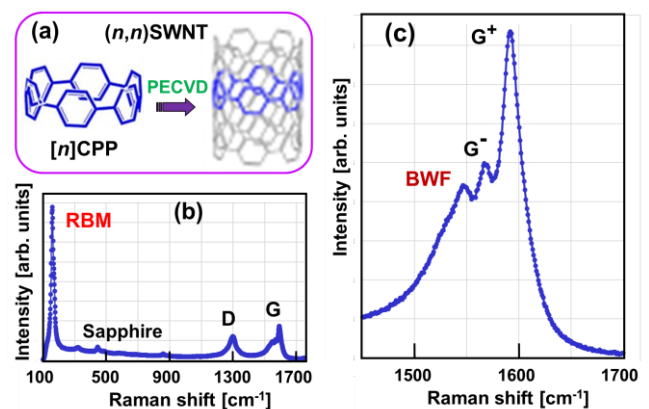


Fig. 1. (a) Molecule structure of  $[n]$ CPP ( $n=6$ ) and expected structure of metallic/armchair SWNT growing from the CPP. Raman spectra of (b)  $[12]$ CPP after PECVD and (c) magnified view around G-band region.

### References

- [1] L. Qiu and F. Ding, *Acc. Mater. Res.* **2**, 828 (2021).
- [2] S. E. Lewis, *Chem. Soc. Rev.* **44**, 2221 (2015).