

VERTICALLY ALIGNED CARPET OF SINGLE-WALLED CARBON NANOTUBES CATALYTICALLY GROWN FROM ALCOHOL

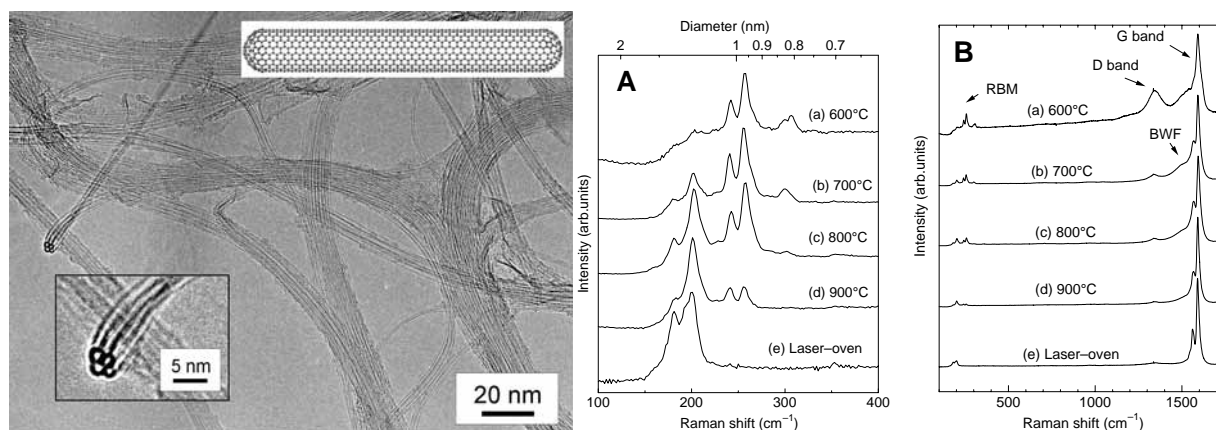
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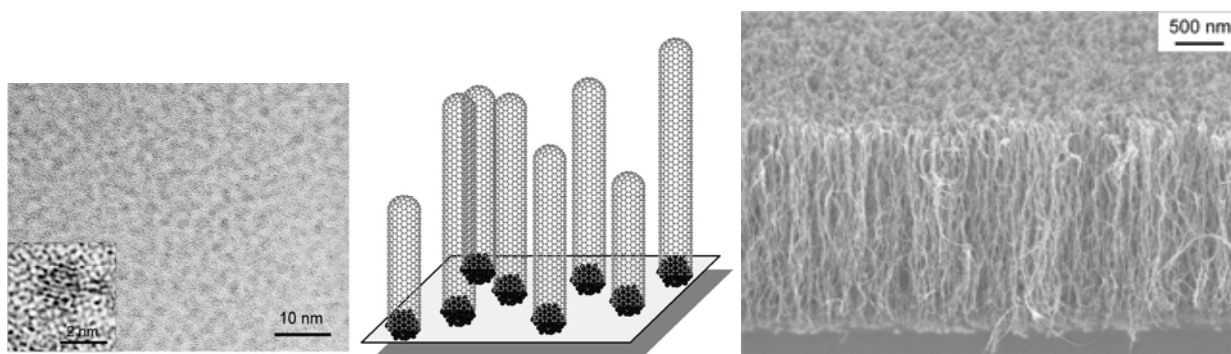
Recent developments of catalytic CVD generation of single-walled carbon nanotubes (SWNTs) by using alcohol as the carbon source are discussed. High-purity SWNTs can be generated at relatively low CVD temperatures from metal catalytic particles supported on zeolite [1, 2] (Fig. 1) or directly dispersed on flat substrates such as meso-porous silica [3], quartz and silicon [4, 5, 6]. Fig. 1 (a) is the TEM image of 'as-grown' sample using this zeolite support method. No metal particles, no multi-walled carbon nanotubes, nor no amorphous carbon are observed. Fig. 1(b) and (c) show Raman scatterings of the sample generated at various CVD temperatures. With decrease in CVD temperature, thinner nanotubes are generated. The zeolite support is used for bulk generation and direct growth on substrates is useful for optical or semi-conductor applications. The zeolite and catalysts metal can be efficiently removed by using HF [7].

By use of the ethanol, the CVD apparatus can be very simple; and the cold-wall CVD with in-situ Raman observation is demonstrated [8]. Recently, the vertically aligned SWNTs mat with a couple of micron meters is grown on quartz substrates by employing the most efficient activation of catalytic metals as shown in Fig. 2 [5, 6]. On the other hand, the chirality distribution of SWNTs determined by the near infrared fluorescence is quite unique for low-temperature CVD condition [9]. The near armchair nanotubes are predominantly generated probably because of the stability of nanotube cap structure for thin nanotubes as shown in Fig. 3 [10]. The growth process of SWNTs simulated by molecular dynamics method [11] gives an important suggestion about this chirality-selective generation of SWNTs. Perspective of chirality-selective CVD generation will be discussed with some experiments using other carbon sources such as fullerene [12].

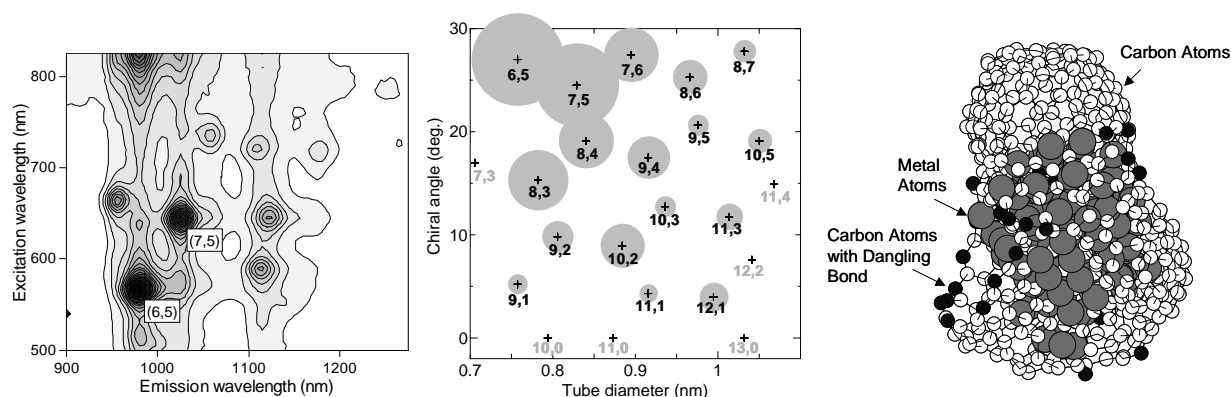
A vertically aligned carpet of single-walled carbon nanotubes (SWNTs) shown in Fig. 2(c) is quite unique. Low-temperature CVD from ethanol (alcohol catalytic chemical vapor deposition, ACCVD) is performed by using densely mono-dispersed Co-Mo catalyst of around 1.0 - 2.0 nm



(a) TEM image of ACCVD sample (b) Raman scattering 488nm(RBM) (c) Raman scattering
Fig. 1 TEM image of Raman scatterings of SWNTs generated from Fe/Co supported on zeolite.



(a) TEM image of catalysts of 1.5 nm (b) Image of growth process (c) Vertically aligned SWNTs mat
 Fig. 2 Generation of SWNTs on flat substrates such as silicon and quartz



(a) NIR fluorescence of SWNTs (b) Chirality distribution (c) Molecular dynamics simulation
 Fig. 3 Chirality distribution by near infrared fluorescence measurement and nanotube cap structure by molecular dynamics simulations

prepared on quartz substrates by a dip-coating method. Fig. 2(a) shows the direct TEM image of Co oxides on the quartz surface just before the CVD reaction. Probably metallic Co nano-particles are responsible to generation SWNTs as in the image in Fig. 2(c). The activation of most of catalyst metal nano-particles is essential for generating dense enough SWNTs with vertical alignment. This activation is achieved by the leak-free CVD chamber or by the continuous reduction of catalysts with Ar/H₂ (3% H₂) gas during CVD. Otherwise, spaghetti-like morphology of SWNTs is obtained. The vertically aligned carpet morphology is clearly demonstrated by anisotropic optical absorption and transmission characteristics in addition to observations by FE-SEM, TEM and resonance Raman scattering.

REFERENCES

- [1] S. Maruyama, R. Kojima, Y. Miyauchi, S. Chiashi and M. Kohno, "Low-Temperature Synthesis of High-Purity Single-Walled Carbon Nanotubes from Alcohol," *Chem. Phys. Lett.*, (2002), vol. 360, no. 3-4, pp. 229-234.
- [2] Y. Murakami, Y. Miyauchi, S. Chiashi and S. Maruyama, "Characterization of Single-Walled Carbon Nanotubes Catalytically Synthesized from Alcohol," *Chem. Phys. Lett.*, (2003), vol. 374, no. 1-2, pp. 53-58.
- [3] Y. Murakami, S. Yamakita, T. Okubo and S. Maruyama, "Single-Walled Carbon Nanotubes Catalytically Grown from Mesoporous Silica Thin Film," *Chem. Phys. Lett.*, (2003), vol. 375, no. 3-4, pp. 393-398.
- [4] Y. Murakami, Y. Miyauchi, S. Chiashi and S. Maruyama, "Direct synthesis of high-quality

- single-walled carbon nanotubes on silicon and quartz substrates," *Chem. Phys. Lett.*, (2003), vol. 377, pp. 49-54.
- [5] Y. Murakami, S. Chiashi, Y. Miyauchi, M. Hu, M. Ogura, T. Okubo, S. Maruyama, "Growth of vertically aligned single-walled carbon nanotube films on quartz substrates and their optical anisotropy," *Chem. Phys. Lett.*, (2004), vol. 385, no. 3-4, pp. 298-303.
- [6] M. Hu, Y. Murakami, M. Ogura, S. Maruyama and T. Okubo, "Morphology and chemical state of Co-Mo catalysts for growth of single-walled carbon nanotubes vertically aligned on quartz substrates," *J. Catalysis*, (2004), vol. 225, pp. 230-239.
- [7] H. Igarashi, H. Murakami, Y. Murakami, S. Maruyama and N. Nakashima, "Purification of Zeolite-Supported High Quality Single-Walled Carbon Nanotubes Catalytically Synthesized from Ethanol," *Chem. Phys. Lett.*, (2004), vol. 392, pp. 529-532.
- [8] S. Chiashi, Y. Murakami, Y. Miyauchi and S. Maruyama, "Cold wall CVD generation of single-walled carbon nanotubes and in situ Raman scattering measurements of the growth stage," *Chem. Phys. Lett.*, (2004), vol. 386, pp. 89-94.
- [9] S. Maruyama, Y. Miyauchi, Y. Murakami and S. Chiashi, "Optical Characterization of Single-Walled Carbon Nanotubes Synthesized by Catalytic Decomposition of Alcohol," *New Journal of Physics*, (2003), vol. 5, pp. 149.1-149.12.
- [10] Y. Miyauchi, S. Chiashi, Y. Murakami, Y. Hayashida and S. Maruyama, "Fluorescence spectroscopy of single-walled carbon nanotubes synthesized from alcohol," *Chem. Phys. Lett.*, (2004), vol. 387, no. 1-3, pp. 198-203.
- [11] Y. Shibuta and S. Maruyama, "Molecular dynamics simulation of formation process of single-walled carbon nanotubes by CCVD method," *Chem. Phys. Lett.*, (2003), vol. 382, pp. 381-386.
- [12] S. Maruyama, Y. Miyauchi, T. Edamura, Y. Igarashi, S. Chiashi, Y. Murakami, "Synthesis of single-walled carbon nanotubes with narrow diameter-distribution from fullerene," *Chem. Phys. Lett.*, (2003), vol. 375, no. 5-6, pp. 553-559.