長尺カーボンナノチューブの合成とリチウム-硫黄電池への応用

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１．　研究課題

Carbon nanotube (CNT) is an important allotrope of low-dimensional carbon materials and exhibits a series of intriguing structure-dependent features. Vertically aligned CNTs, grown on engineered catalyst particles supported on substrates, has attracted extensive attention owing to their excellent carbon purity, tube length and alignment. Chemical vapor deposition (CVD) has been considered as a facile and efficient technology for the mass production of CNTs to meet their large-scale applications. This research focus on the synthesis of high-purity CNTs at high carbon yield using fluidized bed CVD and clarify the influence of synthesis parameters on CNT growth.

２．　主な研究成果

(1) Fluidized bed production of single-wall CNTs (SWCNTs) at high carbon using high concentration C_2H_4

Fluidized-bed CVD is an effective method for the production of CNTs as it benefits from a high surface/volume ratio and efficient heat transfer. Highly active C_2H_2 was typically fed at a low concentration (0.3–1.1 vol%) to prevent deactivation of the active catalyst particles by carbon byproducts and/or tar during CNT growth. Low concentration C_2H_2 requires the use of carrier gas at a high flow rate, resulting in problems associated with heating the reaction gas and significant greenhouse gas (GHG) emissions. Therefore, we substituted low-concentration, highly active C_2H_2 with high-concentration, less active carbon feedstock to reduce the huge GHG emissions. Meanwhile, feeding low-activity carbon feedstocks at high concentrations also enable the high-yield growth of the CNTs, owing to a longer catalyst lifetime originating from the low production rate of carbon impurities.

We achieved the production of vertical-aligned SWCNTs with 0.1 wt%-catalyst impurities using 10–20 vol% ethylene as carbon feedstock and mildly oxidative CO_2 via fluidized-bed CVD. The inhouse-made drum sputtering system is applied to deposit Fe/AlO_x catalyst on the entire surface of ZrO_2 beads (Fig. 1a). By using the catalyst containing 1.4 nm Fe, SWCNTs synthesized using straight FBCVD reactor (Fig. 1b) show array length of 0.4 mm (Fig. 1c) and transmission electron microscope images display the high-purity SWCNTs in the absence of catalyst particles (Fig. 1d). The SWCNTs demonstrates strong RBM peaks and high I_G/I_D ratio of ~5.8 (Fig. 1e) in Raman spectrum but small carbon yield of 5%. The synthesis parameters, including C_2H_4 concentration, annealing time, length of heating zone and size of ZrO_2 beads, were further optimized in order to heat larger amount of beads uniformly using smaller gas flow rate, thus increasing the carbon yield. As a consequence, SWCNTs with an average diameter of 2.9 nm, long length (0.3 mm), low catalyst impurity (0.1wt%, Fig. 1g), and high specific surface area (1178 m^2/g) were obtained at a high carbon yield of 28% (Fig.1f). The effective conversion of high-concentration carbon sources reduces the consumption of additional gases (nitrogen, hydrogen, etc.) and heating power, thus providing a promising method for more efficient and cleaner production of long and pure SWCNTs.

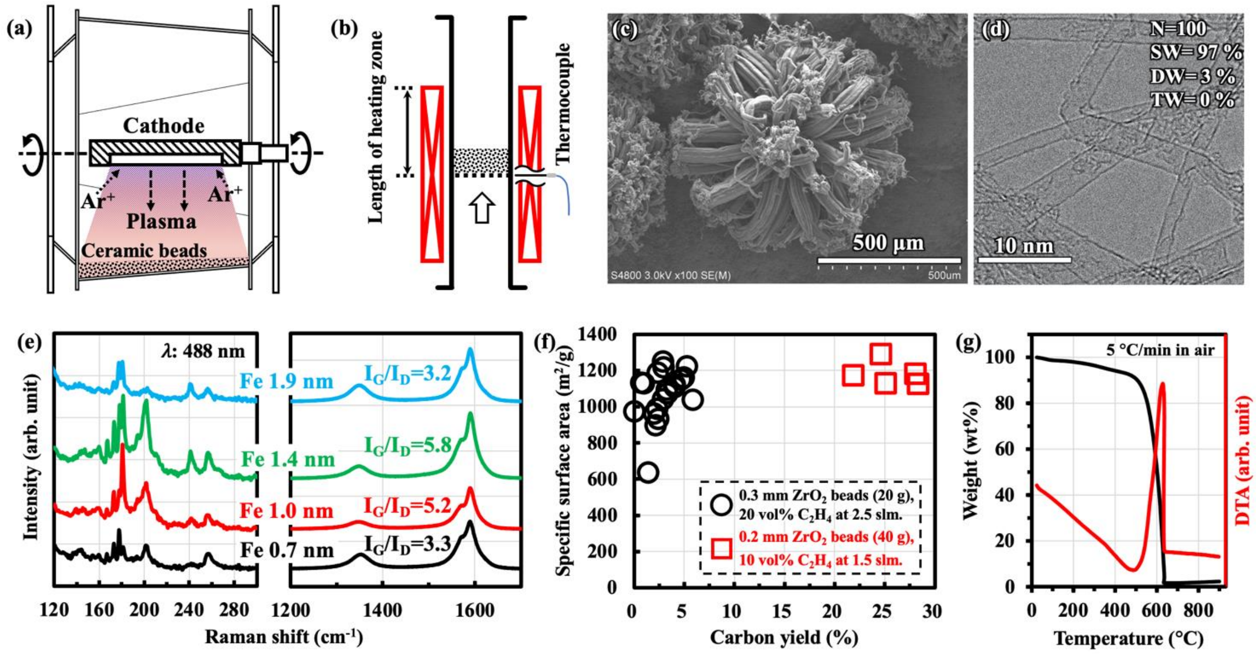

Fig. 1. Schematics of octagonal drum used for sputtering (a), and the vertical reactor used to synthesize SWCNTs via fluidized-bed CVD (b). Scanning electron microscope image (c) and transmission electron microscope images (b) of synthesized SWCNTs on 1.4 nm-thickness Fe. (e) Raman spectra of SWCNTs synthesized at 800 °C for 10 min on Fe with various thickness. (f). Specific surface area and carbon yield of the SWCNTs synthesized using fluidized-bed CVD at 800 °C under various conditions. (g). The thermogravimetry-differential thermal analysis curves of the SWCNTs synthesized with a carbon yield of 28% using 10 vol% C_2H_4, 1 vol% CO_2, and 0.2 mm ZrO_2 beads.

(2) Enhanced CO_2-assisted CVD growth of SWCNT arrays

To further improve the stable and repeatable growth of CNT arrays, we focused on not only the CNT growth during CVD but also the catalyst particle formation during annealing, because the gas environment at annealing stage has significant impacts on the catalyst particle formation and successive CNT growth processes.

We studied the growth of SWCNT arrays by CO_2-assisted CVD with and without feeding CO_2 during annealing and found the significant impact of CO_2 on the formation of catalyst particles. The Fe (1 nm)/AlO_x (15 nm) catalyst is sputter-deposited on SiO_2 (90 nm)/Si substrates. The catalysts annealed without CO_2 yielded CNT arrays with slightly increasing areal mass and arrays height with increasing annealing time (Fig. 2a, c). The height of CNT arrays gradually increased to 1.8–2.2 mm during synthesis with the edge part detaching from the SiO_2/Si substrates (Fig. 2e). However, the catalysts annealed with CO_2 yielded short and straight CNT arrays (Fig. 2b) with decreasing areal mass, array height (Fig. 2d) and growth lifetime (Fig. 2f) with increasing annealing time. These results clearly showed that feeding only small amount of CO_2 at annealing stage has an obvious influence on the growth of CNT arrays. The Fe/AlO_x catalysts that annealed with CO_2 showed stronger Fe 2p peaks (Fig. 2g) and higher oxygen concentration (Fig. 2h) with gradually reduced Fe/Al ratio (Fig. 2i) with increasing annealing time, whereas the catalysts annealed without CO_2 demonstrate weaker Fe 2p peak with similar Fe/Al ratio. These results indicated that Fe catalyst was partially oxidized and the bulk diffusion of Fe into AlO_x layer was enhanced by CO_2. The cross-sectional STEM-EDS images clearly showed the thin and dense Fe layers remained on AlO_x layer after annealing without CO_2 (Fig. 2j, k), whereas Fe diffused into AlO_x layers obviously with overlapped Fe and Al signals on their interface when annealed with CO_2 (Fig. 2l, m). This study emphasized the importance of maintaining a highly reductive atmosphere during catalyst annealing/reduction in order to achieve active catalyst particles with higher number density and longer lifetime.

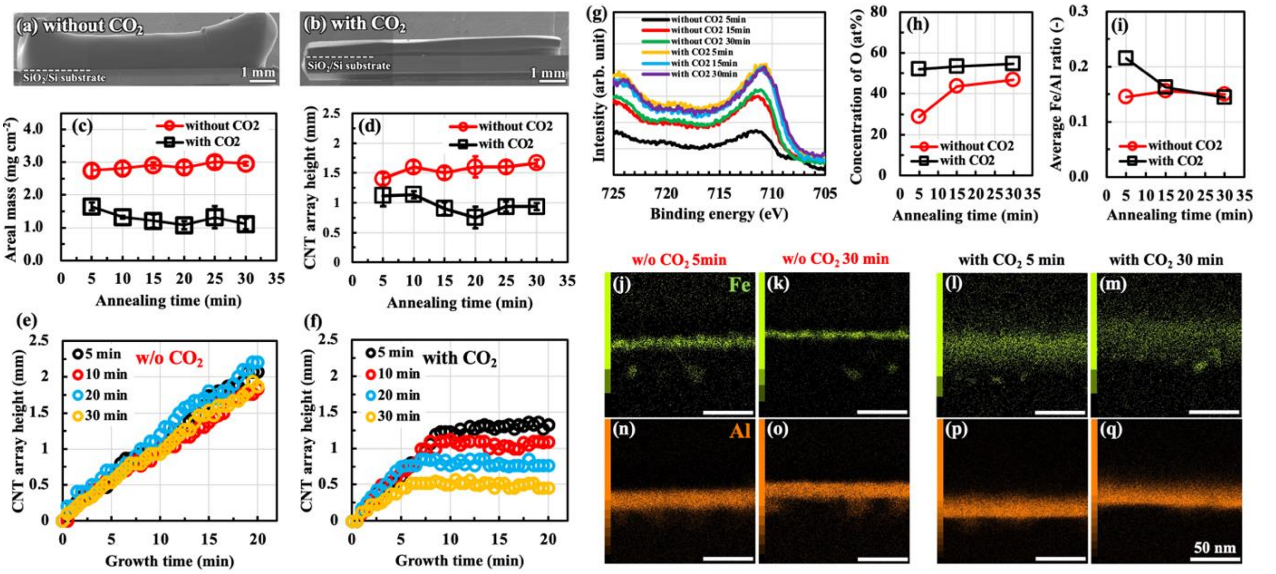

Fig. 2. (a, b) Side-view scanning electron microscopy image, (c) areal mass, (d) average height and (e, f) time profiles of the heights of CNT array that grown for 20 min by Fe/AlO_x catalyst annealed under 10 vol% H_2/Ar without CO_2 (a, c, e) or with 1 vol% CO_2 (b, d, f) at 800 °C for 5–30 min. (g) X-ray photoelectron spectroscopy analysis of Fe 2p spectra of the samples annealed with or without CO_2 for 5–30 min before CNT growth. (h) Average atomic concentration of oxygen. (i) Average Fe/Al ratios. Cross-sectional EDS elemental maps of the 1 nm Fe/20 nm AlO_x catalyst after annealing at 800 °C without CO_2 (j, k, n, o) or with CO_2 (l ,m, p, q) for 5 min (j, n, l, p) and 30 min (k, o, m, q).

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４． 研究業績

4.1 学術論文

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4.2 学会発表

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５． 研究活動の課題と展望

The research about CNT growth will be conducted in the following two aspects. First, the synthesis of high-purity CNTs by feeding high concentration C_2H_4 via fluidized bed CVD will be performed with the assistance of mechanical mixing of beads under small gas flow rate to achieve high carbon yield. Second, the growth of CNTs using fixed bed CVD at high growth rate with long catalyst lifetime by controlling the catalyst diffusion and gas diffusion will be performed.