CO_2-Assisted Chemical Vapor Deposition for Large-Area Synthesis of Carbon Nanotube Arrays

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A small addition of water vapor at 50–200 ppmv level realized millimeter-tall carbon nanotube (CNT) arrays [1]. Its drastic effect is scientifically interesting, however it is practically uneasy to feed the H_2O vapor at the level closed to the background for large-area substrates uniformly. CO_2 can also be an effective additive to remove the excess carbon by the reaction of $C+CO_2 \rightleftharpoons 2CO$. Because CO_2 is milder for oxidation, we propose CO_2 at high concentrations instead of H_2O at low concentrations.

First, we systematically compare the effect of H_2O and CO_2 on the CNT growth with a wide range of Fe thickness (0.20–5.0 nm) using the combinatorial masked deposition (CMD) method [2] on 15 nm Al_2O_x deposited by sputtering on SiO_2/Si substrates [3]. From the threshold Fe thickness (0.20−1.0 nm) for millimeter-tall CNTs (red dotted lines in Figure 1), CO_2 at 0.3–1 vol% proves to have similar effect as H_2O at 50 ppmv. The CO_2 concentration can be roughly 200-fold higher than the H_2O concentration.

Next, we examine the possibility for scale-up of the CNT growth using 50 ppmv H_2O and 1.0 vol% CO_2. 18 substrates (10 mm×10 mm) with 0.80 nm Fe on 15 nm Al_2O_x were loaded in one batch from the inlet to outlet of the reactor. Figure 2 shows change of CNT areal yield with the distance from the inlet. With 50 ppmv H_2O, CNT areal yield decreased dramatically to 0.20 mg/cm^2 for the 4rd substrate (6.0 cm from the inlet). On the other hand, 1.0 vol% CO_2 retained the CNT areal yield at ~1.0 mg/cm^2 for 16 substrates (2–17 cm from the inlet). Therefore, the CO_2 addition at high concentrations is more feasible for the scale-up synthesis of CNT arrays than the H_2O addition at low concentrations.

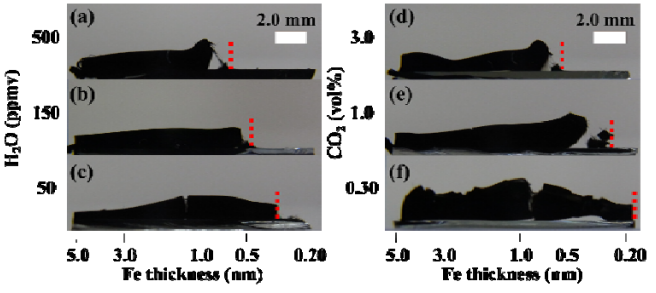

Figure 1. Side-view photographs of CNT forest grown by gradient Fe catalyst on Al_2O_x. H_2O (a–c) and CO_2 (d–f) are used as additive at various concentrations.

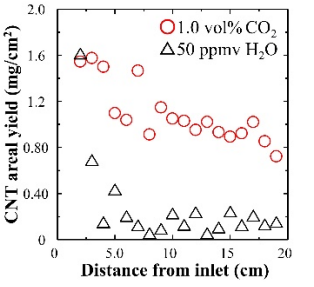

Figure 2. Change of CNT yield with distance from the reactor inlet (△50 ppmv H_2O, ○1.0 vol% CO_2).

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[3] S. Noda, et al., Jpn. J. Appl. Phys. **46**, L399 (2007).

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