Research on aligned carbon nanotubes (ACNTs) has become increasingly popular due to their potential for various applications, e.g. in multiscale devices including energy storage and electronic devices [1–3]. Generally, metal oxide layer (MOL) such as alumina oxide will lead to the growth of ACNTs due to their surface properties [4]. The porous structure of MOL will “trap” catalyst nanoparticle (CNP) during annealing and produce strong adhesion force due to the obtuse contact angle between them. During CNT growth, MOL will act as a core to support CNT alignment and simultaneously prevent CNP lifts off the substrate during initial hydrcarbon deposition and carbon diffusion. Therefore, CNT precipitation is compelled to emerge out of metal’s apex and carbon crystallizes out as hemispherical dome which then extents up in the form of seamless graphitic cylinder. Subsequent hydrcarbon deposition takes place on the lower peripheral surface of the metal, and dissolved carbon diffuses upward. Thus CNT grows up with the catalyst particle rooted on its base [5,6]. Recently, by using simple setup of alcohol catalytic chemical vapor deposition technique, we discovered tip-growth of ACNTs on Co/thermally oxidized Al/SiO₂/Si substrate system using simple alcohol catalytic chemical vapor deposition technique.

In our experiment, Al (25 nm) and Co (7–9 nm) thin films were deposited on Si wafer with a 300-nm-thick SiO₂ layer using radio frequency sputtering physical vapor deposition. The substrate was then placed in a furnace at 400 °C (10 min) for Al thermal oxidation process, followed by annealing for 5 min and CNT growth for 10 min at 700–800 °C using ethanol as carbon feedstock. The whole process was done in the same furnace. A field emission scanning electron microscope (FESEM, 20 kV) and a transmission electron microscope (TEM, 120 kV) were used to characterize the morphology of the ACNTs, respectively.

At growth temperature of 750 °C, ACNTs were successfully grown, and during observation, particles with size 10–20 nm were discovered at the top of the ACNTs, which might indicate the presence of Co CNPs (Fig. 1b). The chemical identity of Co CNPs was then confirmed by the energy-dispersive X-ray spectroscopy (EDX) analysis in Fig. 2 by comparing Co content percentage at different spots. The EDX result clearly showed that the brighter spots contain higher percentage of Co as compared to the dark spots which mainly indicated the presence of carbon (the CNTs). Although there is a slight difference in the growth rate, the tip-growth mode is also observable for T = 700 and 800 °C samples (Fig. 1a and c).

Meanwhile, TEM image further clarify the presence of Co CNPs inside CNTs which indicated the tip-growth mode (Fig. 3) and the presence of ACOr (Fig. 3, right). In this case, we may assume two ideas: (1) the Co CNP diameter, and (2) the formation of ACOr has driven toward tip-growth mode. The interaction between small carbon patches (small polyaromatic sections or reticulated carbon chains) that were supposed to be built after dehydrogenation of...
the first carbonaceous molecules and the CNP surface can be con-
sidered as the key for tip-growth mode. Therefore, large CNP is less
chemically reactive with this carbon patch compared to the smaller
one. In terms of kinetics, we can consider that carbon patches have
adequate time for diffusion on the surface of large CNP before the
formation of complete hemispherical cap. Thus, during CNT
nucleation, the first graphitic sections formed on the surface of
large CNP diffuse quickly to the catalyst/substrate interface and
stabilize it (Fig. 4a). This leaves CNP top surface exposed for further
carbon absorption. This nucleation step leads to the particle
elongation and finally drives the particle lifts off the substrate to
form the tip-growth mode [8]. Meanwhile, the formation of ACOr
will eventually lift off the Co CNPs from MOL at the early stage of
CNT growth. Carbon atom and the graphitic layers were formed
around the surface of the solid CNP and then ACOr was attained
until the catalytic nanoparticle became poisoned [9]. At this stage
the adhesive force between CNP and MOL decreased due to the
formation of ACOr. At some point during ACOr formation, the CNPs
become saturated due to the carbon solubility limit. Even after
ACO or formed, carbon segregation begins which determines the final
CNT product (Fig. 4b).

In summary, there is a possibility for tip-growth to occur with
the influence of the size of CNPs and formation of ACOr on the
CNP surface even with MOL as catalyst support. The cause for ACOr
formation might be the same as nano-onion but still needs further
investigation.

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