

Rapid growth of carbon nanotube forests from ethylene by Fe/Al₂O₃ catalyst: A narrow window and a possible mechanism

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A parametric study was carried out and a growth mechanism was proposed for the rapid growth of carbon nanotubes so-called “super-growth” by Hata, et al [1]. We applied our combinatorial method in which a series of catalyst nanoparticles of different sizes were prepared from a catalyst thickness profile preformed on a substrate [2]. A complicated optimization among catalyst and reaction conditions was needed to find a narrow window for the millimeter-tall nanotube forests. A typical reaction condition was C₂H₄ 60 Torr, H₂ 200 Torr, H₂O 0.076 Torr, Ar balance at atmospheric pressure and 820 °C with a residence time of a few seconds within a tubular hot-wall reactor. The catalyst libraries had Fe (0.5- 10 nm) on Al₂O₃ (20 nm), both of which were sputter deposited on a quartz glass substrate. The tube diameter largely depended on the Fe thickness. The catalyst with 0.9 nm Fe yielded a 1.6-mm-tall, single- and double-walled nanotube forests with a G/D ratio ~ 8 in a 10 min reaction time under the condition above.

The slight addition of H₂O drastically increased the nanotube growth rate while degrading G/D ratio to 8 from 12. It should also be noted that H₂O deactivated catalysts with small Fe loads (i.e. ~ 0.5 nm), where thin nanotubes expectedly forms. The addition of optimum amount of H₂ activated catalyst with moderate Fe loads (i.e. ≥ 0.9 nm) and improved both growth rates and G/D ratios. Higher temperatures led to larger growth rates and G/D ratios but too high temperatures resulted in soot formation. As for catalysts, Co and Ni also had moderate activities when supported on Al₂O₃, but any metal had poor activities when supported on SiO₂.

Considering that alumina and its related materials catalyze hydrocarbon reforming, a possible mechanism is proposed as follows: C₂H₄ or its derivatives adsorb on Al₂O₃, diffuse on its surface to be incorporated into Fe nanoparticles, and segregate as nanotubes from Fe nanoparticles. H₂O makes/keeps Al₂O₃ surface reactive, and H₂ controls the balance of hydrogenation/dehydrogenation of surface carbon species. The boost of carbon incorporation into Fe by Al₂O₃ drastically increases the nanotube growth rates, but degrades the nanotube quality and deactivates small Fe catalysts. There should be a plenty of rooms in supporting materials for the further development of supported catalysts for nanotubes.

[1] K. Hata, et al., *Science* **306**, 1362 (2004).

[2] S. Noda, et al., *Appl. Phys. Lett.* **86**, 173106 (2005); *Carbon* **44**, 1414 (2006).

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