# Combinatorial Control of Catalyst for Basics and Applications of Carbon Nanotube Growth

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Control of catalyst nanoparticles is a key for further progress in both SWNT production and understanding of its growth mechanism. We have developed "combinatorial masked deposition (CMD)" method [1], in which a series of catalyst nanoparticles are formed on a substrate from a catalyst gradient thickness profile preformed by sputtering through a physical filter. We have applied this CMD to alcohol catalytic CVD (ACCVD) [2] and realized SWNT films by $Co/SiO_2$ [3] and $Ni/SiO_2$ [4], and VA-SWNTs by $Co\text{-}Mo/SiO_2$ [5].

This time we studied ACCVD in detail. $Co/SiO_2$ grew SWNTs and MWNTs efficiently at Co thickness of 0.1-0.2 nm and 1-2 nm at 973 K, respectively, and hardly grew nanotubes in between. $Co\text{-}Mo/SiO_2$ yielded VA-SWNTs under several conditions, including Co/Mo atomic ratio of (i) 1/2 reported for CO disproportion [6] and (ii) 1.6/1 for ACCVD [7] (Fig. 1). We also found the third region with pure Co (iii) highly efficient under 4 kPa $C_2H_5OH$, yielding VA-SWNTs with a bimodal diameter distribution. Catalyst layers of different thickness yield different particles, which are catalytically active for different conditions.

We also applied CMD to "supergrowth [8]" and reproduced it [9]. Figure 2 shows a millimeter-thick forest grown in 10 min by 0.2-3-nm-thick Fe on $Al_2O_x/SiO_2$. Thin Fe (~ 0.5 nm) yielded SWNTs under a limited condition, and thicker Fe yielded thicker nanotubes under wider conditions. CMD enabled efficient optimization because CVD condition can be adjusted to lead the threshold Fe thickness for VA-CNTs smaller. Aluminum oxide, which is a well-known catalyst in hydrocarbon reforming, had an essential role in enhancing the nanotube growth by dissociating carbon species and supplying them to Fe nanoparticles.

SWNT growth at a low areal density is important as well. The as-grown network of thick bundles resulted from sparse, long SWNTs (Fig. 3a) by ACCVD showed a transparent conducting property much better than that of thin bundles from short, dense SWNTs (Fig. 3b).

In summary, there remains abundant potential in catalytic growth of nanotubes and CMD is effective in both understanding and developing supported catalysts.

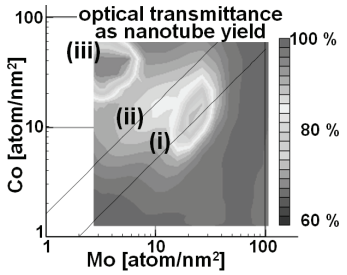


Fig. 1. Co-Mo activity map.

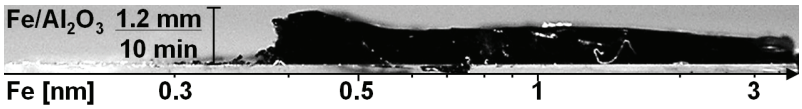


Fig. 2. SWNT "supergrowth" reproduced by CMD catalyst.

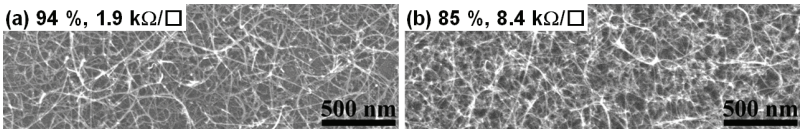


Fig. 3. Transparent conducting films of as-grown SWNTs.

[1] S. Noda, et al., *Appl. Surf. Sci.*, **225**, 372 (2004). [2] S. Maruyama, et al., *Chem. Phys. Lett.*, **360**, 229 (2002). [3] S. Noda, et al., *Appl. Phys. Lett.*, **86**, 173106 (2005). [4] K. Kakehi, et al., *Chem. Phys. Lett.*, **428**, 381 (2006). [5] S. Noda, et al., *Carbon*, **44**, 1414 (2006). [6] J.E. Herrera, et al., *J. Catal.*, **204**, 129 (2001). [7] Y. Murakami, et al., *Chem. Phys. Lett.*, **385**, 298 (2004). [8] K. Hata, et al., *Science*, **306**, 1362 (2004). [9] S. Noda, et al., *Jpn. J. Appl. Phys.*, **46**, L399 (2007).

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