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Combinatorial Control of Catalyst Nanoparticles for Customized Production of Single- and Multi-Walled Carbon Nanotubes

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1. Introduction

Various applications have been proposed and researched for carbon nanotubes but the practical use is quite limited. In Fig. 1, applications are mapped against the degree of structural control and the added value of devices. To realize high-end application such as field-effect transistors, nanotubes need to be single-walled (SWNTs) with controlled chirality, and need to be precisely positioned at a large scale. Such precise controls of individual SWNTs are still major challenges. To realize applications such as polymer composites and electrodes of batteries/capacitors, breakthrough is needed in the cost and scale of nanotube production. Electronic/electric devices such as via-filling, field-emitters, and transparent electrodes can be placed in between. They do not require such precise controls of individual nanotubes and mass production of nanotubes. Instead, how to control their ensemble structure and how to realize them at a large area uniformly at a high throughput become important. To realize practical use of nanotubes, development of the production process customized for each application should be crucial.

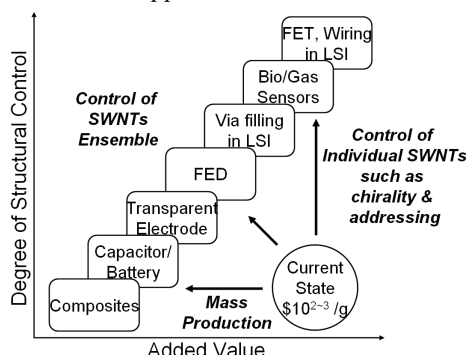


Fig. 1 Mapping of CNT applications.

For such customized production processes, the control of catalyst nanoparticles for nanotube growth is important. We have developed a method named "combinatorial masked deposition, CMD [1]", in which a series of catalyst nanoparticles can be obtained on a substrate by simply annealing gradient thickness profiles of catalysts preformed by sputter-deposition using a physical filter. Nanotubes growing at different areal densities on a substrate resulted into different ensemble structures such as sparse individual SWNTs and bundled SWNT networks [2]. The flexible nature of thin nanotubes (a few nm in diameter) makes such nanotubes self-organize into various ensemble structures. In

this work, we applied our CMD method for the rapid growth of vertically aligned SWNT forests (VA-SWNTs) and for the bundled SWNT networks for transparent electrodes.

2. Support enhanced rapid growth of VA-SWNTs

When SWNTs grow at a high areal density $\sim 10^{16} [\text{m}^{-2}]$, they self-organize into VA-SWNTs. Soon after the discovery of this phenomenon [3] during alcohol CVD [4], several groups have realized this structure by different methods. Among them, the water-assisted method so-called "supergrowth" realized an outstanding growth rate of a few $\mu\text{m/s}$, thus yielding millimeter-thick VA-SWNTs [5]. However, few groups have reproduced it and we carried out a parametric study for it [6].

Figure 2 briefly shows the experimental procedure. A gradient thickness profile of Fe (0.2- 3 nm) was formed on an Al_2O_3 layer, which was preformed on a quartz glass substrate. This catalyst library was set in a tubular, hot-wall CVD reactor (22-mm inner diameter), heated up under $\text{H}_2/\text{H}_2\text{O}/\text{Ar}$ flow, and CVD was carried out by flowing 8.0 kPa $\text{C}_2\text{H}_4/27$ kPa $\text{H}_2/0.010$ kPa $\text{H}_2\text{O}/67$ kPa Ar at a flow rate of 500 sccm at 1093 K for 10 min. Millimeter-thick nanotube films grew up.

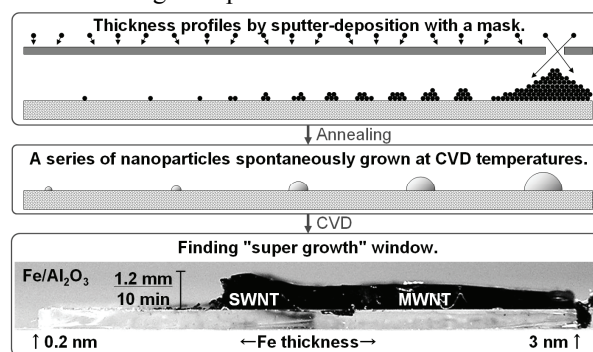


Fig. 2 Schematic of CMD method and a photograph of resulted VA-CNTs of a series of diameters.

Figure 3(a) shows an TEM image of the as-grown sample for 0.5 nm Fe thickness. Nanotubes were mainly SWNTs. "Supergrowth" of VA-SWNTs was reproduced. Figure 3(b) shows Raman spectra taken at different Fe thicknesses. The G/D peak area ratio of 10 for 0.5 nm Fe thickness was somewhat better than those of original "supergrowth" [5]. The G/D ratio decreased as the Fe thickness increased (0.8- 1.0 nm), because of the increased

nanotube diameter.

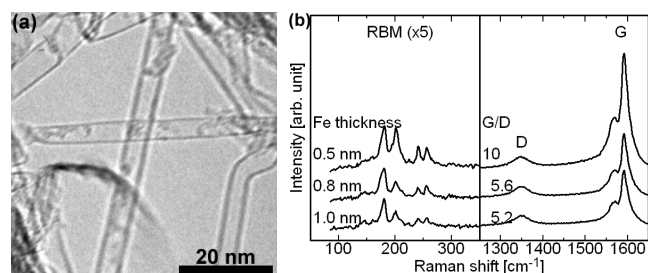


Fig. 3 An TEM image (a) and Raman spectra (b) of our millimeter-thick nanotubes.

It should be noted that the window for the rapid growth is wide for thick nanotubes at large Fe thicknesses (≥ 1 nm), while it is quite narrow for SWNTs at small Fe thicknesses (~ 0.5 nm). H_2 apparently plays an important role in the rapid SWNTs growth as well as H_2O . It should also be noted that this kind of rapid growth occurs only when Fe is supported on an Al_2O_3 underlayer and that the Al_2O_3 underlayer can enhance the nanotube growth also by Co and Ni catalysts. The catalytic role of Al_2O_3 in hydrocarbon dissociation, which has long been known in hydrocarbon reforming [7], should be essential in "supergrowth".

3. As-grown SWNT network as transparent electrodes

Transparent electrodes are a candidate application of SWNTs [8]. SWNT films of various structures have been made, and the matrix-free SWNT films show much better performance than those with conducting polymers as matrix. Direct connection between SWNTs apparently has the minimal contact resistance. For this viewpoint, as grown SWNT films should be ideal. Because SWNTs usually contain twice as much semiconducting ones as metallic ones, how to reduce the contribution of the former to the resistivity is important. n -times longer SWNTs grown at a $1/n$ -times lower areal density have a $1/\sqrt{n}$ -times smaller inter-spacing, thus expectedly form thicker bundles, in which SWNTs are connected rather in parallel. Metallic SWNTs will govern the resistance and the lower sheet resistance is expected.

Because a variety of catalysts can be prepared for binary systems, SWNT networks were grown by using a Co-Mo catalyst library from alcohol [10]. Different values have been reported as the optimum atomic ratio for CO (1/2-1/3 [9]) and ethanol (1.6/1.0) [3], and in addition to them, we recently found the third condition where pure Co grew VA-SWNTs rapidly at a high ethanol pressure (4.0 kPa) (Fig. 4a). Then we set two conditions; 0.12 nm Co/0.34 nm Mo at 0.40 kPa ethanol for 3 min for short SWNTs at a high areal density (A) and 0.5 nm Co without Mo at 4.0 kPa ethanol for 10 min for long SWNTs at a low areal density (B), both of which are grown on quartz glass substrates at 1073 K. As expected, a coarser SWNT network was obtained for the latter, and showed a 94 % optical transmittance and a 1.9 $k\Omega/\square$ sheet resistance, which is 8-times better than the former (Fig. 4b). Structures and properties of nanotube films can be tailored in this way.

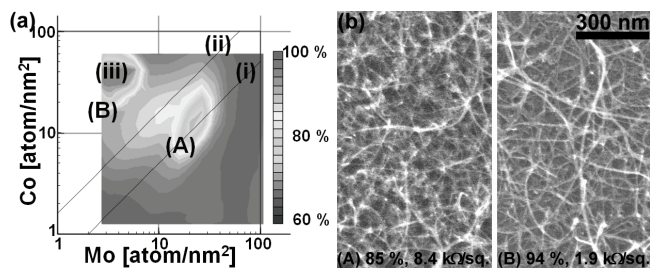


Fig. 4 (a) Relative nanotube yields (optical transmittance) mapped against Co-Mo concentrations. Catalyst thickness was 0.01-0.8 nm and 0.04-2.3 nm for Co and Mo, respectively. (b) SEM images of as-grown SWNT network films and their properties.

4. Conclusions

Because the requirements for nanotubes vary so much, production processes customized for each application should be crucial for the practical use of nanotubes. The flexibility of nanotubes with narrow diameters enables such nanotubes self-organize into various ensemble structures. Control of catalyst nanoparticles should be the key in controlling such phenomena. Examples were shown for the rapid growth of VA-SWNTs and the SWNT networks for transparent electrodes by preparing a variety of catalysts using our CMD method. The nominal thickness of catalyst metals as well as the catalytic activity of catalyst supports proved important. There should be a plenty of rooms in further development of supported catalysts.

Acknowledgements

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