

## Growth of carbon nanotubes on carbon nanofibers

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### Introduction

CNTs, which have extremely small diameter and high aspect ratio, have superior electrical and thermal conductivity and mechanical strength. CNTs are expected to be used as functional filler to improve the conductivity and mechanical properties of plastics and ceramics. In this study, we develop three-dimensional CNT@CNF by growing CNTs on carbon nanofibers, which are expected to further improve electrical conductivity and strength in composites as well as in electrode.

### Experimental

CNFs(VGCF, Shouwa Denko) with average diameter of 150 nm and fiber length of 10-20  $\mu\text{m}$  were used. Catalyst particles for growth of CNTs were adhered on CNFs by two methods. In surfactant method, catalytic precursor solution consisted of Co nitrate or Ni nitrate with addition of dodecylbenzenesulfonic acid(DBA) or dodecylsodium sulfate (SDS). CNFs were dispersed the precursor solution and filtered by anodized alumina membrane. In chemical precipitation process, the CNFs, which were treated in  $\text{HNO}_3$  at  $110^\circ\text{C}$  for 2h, were dispersed in aqueous solution of Co nitrate. Ammonia solution was added into the solution to adjust pH value to 9.5. The CNFs were then separated and washed using centrifuge. The growth of CNTs on CNFs was carried out at  $600^\circ\text{C}$  for 20 min in  $\text{N}_2$ ,  $\text{H}_2$  and  $\text{C}_2\text{H}_2$ .

### Result and discussion

Fig. 1(a, b) shows the images of CNTs grown on CNFs from Co-DBA and Ni-SDS catalyst precursors. It can be seen that CNTs formed around the CNFs. The average diameter of CNTs from Co-DBA is 18 nm, and that of CNTs from Ni-SDS is 15 nm. Since DBA and SDS is anion surfactant, hydrophilic group is ion exchanged by  $\text{Co}^{2+}$  or  $\text{Ni}^{2+}$  while hydrophobic group adhered on CNFs surface. After drying and decomposition, small nanoparticles were formed on the CNF surface. However, CNFs aggregated severely due to the presence of DBA or SDS.

Fig. 1(c, d) shows the images of the catalyst particles obtained by chemical precipitation process, and the corresponding CNTs. The CNTs showed higher growth density than those obtained from Co-DBA and Ni-SDS. The CNTs has average diameter of 20 nm and CNT@CNF has maximum diameter of 750 nm. From Fig. 1c, it is seen that many nanoparticles adhered on the surface of CNF. The precipitation of cobalt

hydroxide generated by pH adjustment combined with - OH and - COOH of the CNFs surface, and thus the nanoparticles adhered to CNFs [1].

Fig. 2 shows the comparison of the catalyst particles and CNTs when Co-DBA or chemical precipitation process was used. The average catalyst particle size after reduction for Co-DBA was 22 nm, while the catalyst particle size for chemical precipitation process was 12 nm. It indicates that the chemical precipitation process is more adequate method to synthesize small and uniformly-distributed nanoparticles on CNFs.

Although the catalyst particles obtained from chemical precipitation process was smaller, the CNTs had similar diameter to those from Co-DBA. It is probably because many large particles did not contribute to the growth of CNTs in Co-DBA. Both kinds of CNTs had the curved morphology.

### Conclusions

Treatment in Co-DBA or Ni-SDS precursor solution could adhere nanoparticles on CNFs. However, chemical precipitation process was a better method to adhere catalyst particles on CNFs, and CNTs with high growth density were formed on CNFs.

### Reference

[1] Z. Dong, K. Ma, K. He, Mater. Lett 62 (2008) 4059-4061.

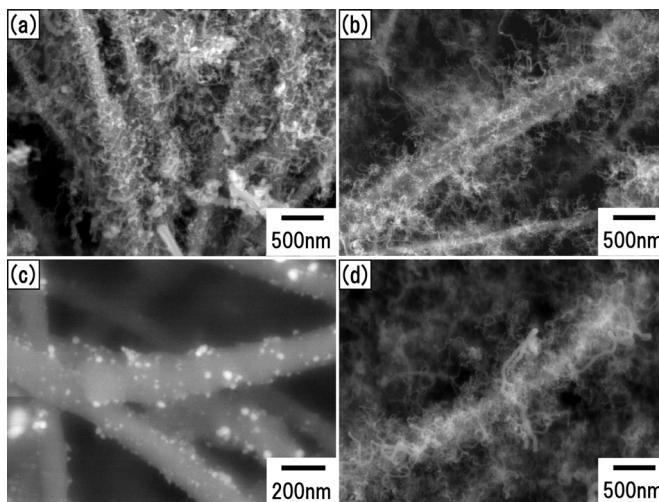


Fig.1. SEM images of CNTs grown on CNFs by Co-DBA (a) and Ni-SDS (b) treatment, (c) Co catalyst adhered on CNFs by chemical precipitation process, (d) CNTs grown from (c).

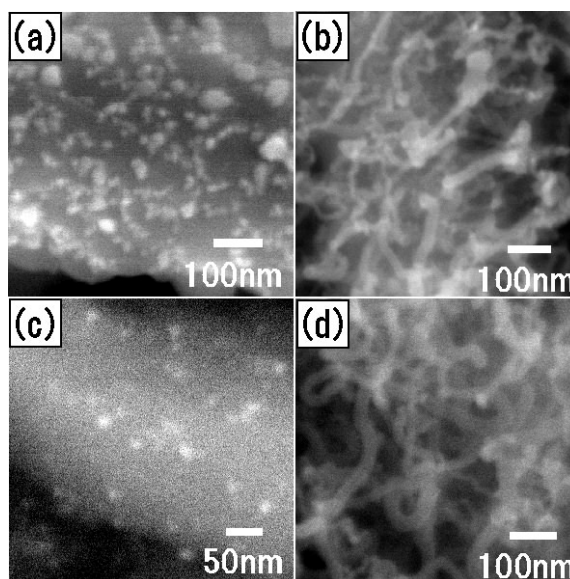


Fig2. SEM images of (a)Co catalyst obtained by Co-DBA, (b) CNTs synthesized from (a), (c) Co catalyst obtained by chemical precipitation process, and (d) CNTs synthesized from (c).