Effect of high-temperature annealing on N-doped nanotube structures and oxygen reduction reaction (ORR) catalytic activity

Carbon nanotubes have many applications including catalyst supporting media, electrochemical energy storage, and oxygen reduction reaction (ORR) catalyst for fuel cells. In this presentation, N-doped MWCNTs (CN_x-MWNTs) are synthesized by a floating catalytic chemical vapor deposition (CVD). TEM, XRD, XPS, and electron energy-loss spectroscopy (EELS), have been performed to study the CVD-derived nanotube microstructures and N-doping of both as-produced CN_x-MWNTs and high-temperature annealed CN_x-MWNTs. At an annealing temperature of 1600 °C, Fe_3C particles grow into larger particles, consisting of Fe_3C, α-Fe, and γ-Fe. These metal catalyst particles are completely removed from the nanotubes after heating to 2800 °C, which also anneals lattice defects resulting in improved crystalline order and facetted polygonal nanotube cross sections.

ORR rotating disk electrode measurements show that as-prepared CN_x-MWNTs have better catalytic activity than thermally annealed MWCNTs. The as-prepared CN_x-MWNT sample achieves ORR onset potential of -0.05 V (vs Ag/AgCl) and the highest current density, which follows a 4-electron process indicating the reduction of oxygen to water. The nanotube sample annealed at 2800 °C, shows the highest onset potential of -0.20 V (vs Ag/AgCl), the lowest current density indicating low activity, and an average electron transfer number of 2 converting oxygen to hydrogen peroxide. The nanotube sample annealed at 1600 °C, exhibits intermediate ORR performance between as-prepared CN_x-MWNTs and the MWNTs annealed at 2800 °C. These results indicate that the ORR performance is distinct and well correlated with the amount of nitrogen-doping and iron nano-particles within each sample, which agrees with XPS and EELS analysis results.