CO_2 Enhanced Carbon Nanotube Synthesis from Pyrolysis of Hydrocarbons

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Supporting Information

1) CO_2-assisted single wall carbon nanotube synthesis

The Fe-Mo/MgO catalyst was prepared by an impregnation method. An iron nitrate hydrate ($Fe(NO_3)_3 \cdot 9H_2O$) and ammonium molybdate ($(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) solution with MgO powder was ultrasonicated to form a gel, dried at 110 ^oC, ground to a fine powder, and then calcined at 500 ^oC for 3 hours. The weight ratio of Fe/Mo/MgO in the catalyst was 1:1:40. Around 100 mg of the catalyst was uniformly spread into a thin layer under argon flow at 200 mL/min on a graphite susceptor and placed at the center of a quartz tube positioned horizontally inside an inductive furnace. After purging the system with argon as carrier gas for 10 minutes, radio frequency (RF) heating at 350 kHz was applied to the graphite susceptor that contains the catalyst. The catalyst was first reduced with hydrogen (20 mL/min) at 720 ^oC for 30 minutes. The synthesis of SWNTs was performed at 900 ^oC by the introduction of methane (50 mL/min) and CO_2 (0 - 50% related to that of methane) for about 30 minutes. The CVDs were carried out at pressure of about 1 atm. The carbon source was diluted by argon in order to decrease the contact time between the carbon feedstock and the catalyst, and consequently reduce the formation of amorphous carbon. Neither nanotubes nor any other types of carbon byproducts were found in the experiments performed only with a graphite susceptor without catalyst. The as-produced CNTs were purified in one easy step using diluted hydrochloric acid solution (1:1 v/v) under sonication for 2 hours, followed by distilled water wash and drying at 120 ^oC overnight.

2) GC/MS analysis:

The components of the exhaust gas from the reaction were quantified with an Agilent 6890/5975C GC/MS system. The proprietarily designed gold quartz quadrupole enhances performance and reliability up to 1050 u. The new Trace Ion Detection technology lowers detection limits in complex matrices and enhances baseline reproducibility. The MS spectra were taken under $6x10^{-6}$ torr.

3) CO_2-assisted MWNT growth from pyrolysis of acetylene on Fe-Co/$CaCO_3$ catalysts

Catalyst preparation: The stoichiometric composition of the catalyst was Fe:Co:$CaCO_3$ = 2.5:2.5:95 wt%. First, the weighted amount of metal salts $Fe(NO_3)_3 \cdot 9H_2O$ and $Co(CH_3COO)_2 \cdot 4H_2O$ were dissolved into distilled water with agitation, and $CaCO_3$ was added to the solution after the metal salts were completely dissolved. The pH-value of the mixture solution was adjusted to about 7.0 by dipping ammonia solution, in order to avoid the release of CO_2 occurring when carbonates contact acids. Then, the water was evaporated with a steam bath under continuous agitation, and the catalyst was further dried at about 130 ^oC overnight.

MWNT synthesis: Carbon nanotubes were synthesized on the Fe-Co/$CaCO_3$ catalyst with cCVD approach using acetylene as carbon source. About 100 mg of the catalyst was uniformly spread into a thin layer on a graphite susceptor and placed in the center of a quartz tube with inner diameter of 1 inch, which is positioned horizontally inside a resistive tube furnace. Heating was applied after purging the system with argon at 200 mL/min for 10 minutes, and acetylene was introduced at 4.3 mL/min for about 30 minutes when the temperature reached around 720 ^oC. These flow rates correspond to a linear velocity of the gas mixture inside the reactor of 40 cm/min. Therefore it takes approximately 14 seconds for the acetylene/argon mixture to travel from one side to the other one of the 9 cm long catalyst bed.