A NOVEL CARBON NANOTUBES SYNTHESIS CONTINUOUS PROCESS USING IRON FLOATING CATALYST ON MGO PARTICLES FOR CVD OF METHANE IN A FLUIDIZED BED REACTOR

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Abstract

A novel continuous process was employed for synthesis of carbon nanotubes (CNTs) by catalytic chemical vapor deposition (CCVD) of methane over Fe/MgO using a combination of a fluidized bed reactor and a floating catalyst. MgO, fluidized by methane as the carbon source, was transferred to top of the hot zone of a fluidized reactor, where ferrocene vapor was introduced. Ferrocene decomposes in the reactor hot zone and iron nanoparticles deposit on the MgO. CNTs are grown by CCVD of methane on the in-situ produced Fe/MgO catalyst, on its flow along the reactor. More efficient contact of the ferrocene and MgO was obtained by placing an annular tube in the ferrocene-MgO contact region. CNTs are only grown when the MgO as the support was introduced into the reactor. Dense entangled bundles of 20-30 nm CNTs with Raman I_G/I_D of about 10, indicating high quality CNTs with low amorphous carbon impurities, were obtained when the annular contactor was used.

Introduction

Carbon nanotubes (CNTs) have attracted considerable attention since their discovery by Ijima in 1991, due to their outstanding physical and chemical properties. Various synthesis methods have been developed for the production of CNTs, including electric arc discharge, laser vaporization, and catalytic chemical vapor deposition (CCVD). Many previous reports have shown the possibility of CNTs production by CVD method on a large scale at a very low cost.

Different types of reactor configurations including the fixed bed micro-reactor or small fluidized-bed reactors with short contact times have been employed for the CCVD synthesis of CNTs. "Fixed bed", "floating catalyst", and "fluidized bed" are the most common processes for the CCVD growth of CNTs.

The efficiency of the CNTs growth in the fixed-bed process is limited severely by inhomogeneous gas-solid mixing across the catalyst bed, with the dense packing of the catalyst particle preventing both CNTs production and dissipation of the by-products. This situation is worsened by the growing nanotubes forming a mat that covers the catalyst bed. These problems can be solved by fluidizing the catalyst particles. A recent research demonstrated that in the nano-agglomerated fluidized bed reactor, sufficient growing space, uniform temperature and concentration distribution and good mass and heat transfer lead to uniform CNTs with high yield.

In this work, we report a novel continuous method for large-scale production of CNTs. This method is based on CCVD of methane using a combination of floating catalyst and fluidized bed reactor.

Experimental

The CNTs synthesis system comprises of two main parts of a fluidized bed quartz reactor and ferrocene injection equipment. A small diameter quartz tube inside the reactor transfers MgO powder, fluidized by methane as the CNTs synthesis carbon source, to the top of the hot-zone of reactor. Ferrocene was sublimed in a chamber heated to 150°C and transferred into the reactor by a helium flow. The ferrocene vapor was introduced on top of the small inner tube to provide its most efficient contact with MgO powder in the hot zone of the reactor. A cooling system prevents overheating and decomposition of ferrocene in its transfer line to the reactor. The CNTs synthesis temperature was varied in the range of 900 to 1000°C. CNTs were characterized by SEM and Raman spectroscopy.

Results and discussion

Figures 1a and 1b show SEM micrographs of the CNTs samples synthesized in the absence and the presence of MgO, respectively. Fig. 1 reveals that CNTs are grown only in the presence of MgO as the support. The contact of MgO particles with ferrocene provides a large surface area for deposition of the iron nanoparticles required for the CNTs growth.

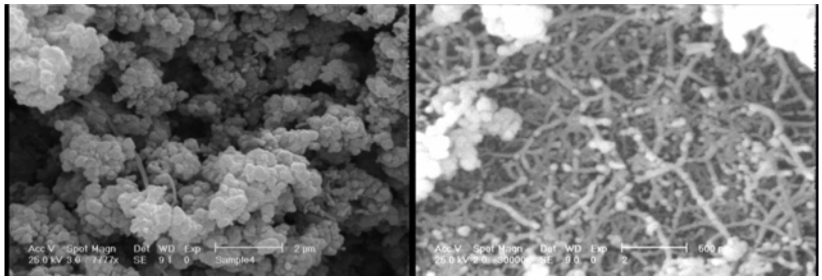

Figure 1- SEM micrograph of CNTs grown by the CCVD of methane at 950^{o}C a) in absence of MgO, and b) in presence of MgO as the support.

Figure 2 represents the CNTs grown on MgO at the same conditions as in Fig. 1, but when the annular tube was used around the ferrocene transfer line and the top of inner tube transferring the MgO powder to the reactor. A highly dense entangles of CNTs with an IG/ID ratio of about 10, indicating high quality CNTs, are obtained. The annular tube may provide a more efficient contact of the ferrocene and MgO leading to higher density of iron nanoparticles of smaller sizes.

Not shown here, as more ferrocene is introduced to the reactor higher yields of CNTs are obtained. Furthermore, higher quality CNTs are obtained at lower temperatures.

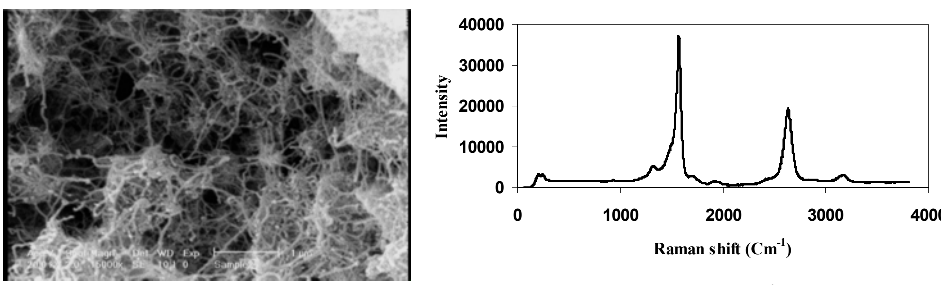

Figure 2- a) SEM micrograph of CNTs grown by CCVD of methane at 950^{o}C using the annular tube, b) its Raman spectrum

Conclusion

Carbon nanotubes are synthesized in a novel fluidized-bed reactor using ferrocene as the floating catalyst and MgO as the support, both of which introduced into the hot zone of the reactor. CNTs are grown only in presence of the MgO support, confining the ferrocene and MgO contact space leads to higher density of CNTs with high quality. This may be due to a more efficient contact of ferrocene and MgO that results in higher density of iron nanoparticles of smaller sizes.

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