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A novel continuous process for synthesis of carbon nanotubes using iron floating catalyst and MgO particles for CVD of methane in a fluidized bed reactor

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ABSTRACT

A novel continuous process is used for production of carbon nanotubes (CNTs) by catalytic chemical vapor deposition (CVD) of methane on iron floating catalyst in situ deposited on MgO in a fluidized bed reactor. In the hot zone of the reactor, sublimed ferrocene vapors were contacted with MgO powder fluidized by methane feed to produce Fe/MgO catalyst in situ. An annular tube was used to enhance the ferrocene and MgO contacting efficiency. Multi-wall as well as single-wall CNTs was grown on the Fe/MgO catalyst while falling down the reactor. The CNTs were continuously collected at the bottom of the reactor, only when MgO powder was used. The annular tube enhanced the contacting efficiency and improved both the quality and quantity of CNTs.

The SEM and TEM micrographs of the products reveal that the CNTs are mostly entangled bundles with diameters of about 10–20 nm. Raman spectra show that the CNTs have low amount of amorphous/defected carbon with I_G/I_D ratios as high as 10.2 for synthesis at 900 °C. The RBM Raman peaks indicate formation of single-walled carbon nanotubes (SWNTs) of 1.0–1.2 nm diameter.

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1. Introduction

Carbon nanotubes (CNTs) have attracted considerable attention since their discovery by Iijima in 1991 [1] due to their outstanding physical and chemical properties. Various synthesis methods have been developed for the production of CNTs, including electric arc discharge [2], laser vaporization [3], and catalytic chemical vapor deposition (CVD) [4–7]. High quality CNTs can be synthesized by the first two methods, but they are not adaptable to industrial production. CVD method appears to be the most promising method for large-scale production of CNTs due to its lower reaction temperature and lower cost [8].

Different metal catalysts such as Fe, Co, Mo, Ni and supports like MgO, SiO_2, Al_2O_3, CaO and ZrO_2 have been utilized in the CVD method [9,10]. Iron is one of the common active metals for the CNTs growth and has been investigated by different research groups [11,12]. The growth of CNTs was reported to be easier over Fe catalysts, because with Fe the interaction between formed carbon and metal particles is apparently less structure sensitive than other catalysts for CNTs growth [13]. Furthermore, MgO presents the advantage over other supports. It may be digested within a mild acid environment without damaging the CNTs [14,15].

"Fixed bed", "floating catalyst", and "fluidized bed" methods are the most common processes for the CVD growth of CNTs [16]. The efficiency of CNTs production in the fixed-bed reactor is severely limited by inhomogeneous gas–solid mixing along the catalyst bed, with the dense packing of the catalyst particle preventing CNTs production.

This situation is worsened by the growing CNTs forming an overlay that covers the catalyst particles which results in a decrease in the catalyst activity. These problems may be solved by fluidizing the catalyst particles in a confined reactor by using a gaseous carbon source heated to the synthesis temperature [16,17]. In a fluidized bed reactor, sufficient growing space, and proper mass and heat transfer lead to much higher quality and yield, uniform properties, and relatively perfect micro-structures of grown CNTs [18]. Many researchers prefer to produce CNTs in large scale by utilizing fluidized bed reactors [18–23].

Floating catalyst (or gas phase or aerosol synthesis) method is a kind of pyrolysis method in which the catalyst are carried into the reactor with the liquid carbon source and, like fluidized bed reactor, can be used as a continuous method for large-scale production of CNTs [24–28]. The catalyst particles are suspended in gas phase throughout the entire CNT formation process. The most important advantage of this method is the control of the catalyst particle size by varying the concentration of metal precursor in the solution.

Use of supports such as MgO in CNTs synthesis is crucial for dispersing, stabilizing, and preventing sintering and agglomeration

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of the catalyst nanoparticles. Thus, the growth of CNTs in the floating catalyst method appears to be more difficult to control, due to the absence of a support to prevent the coalescence of the metal catalyst [16].

In this study, advantages of both CVD in a fluidized bed reactor and a floating catalyst method are taken for a novel continuous production of CNTs using methane as the carbon source. Fe nanoparticles as the catalyst are continuously formed by decomposition of ferrocene. MgO particles as a high surface area support are also continuously introduced into the reactor which prevents the iron nanoparticles from agglomeration, resulting in smaller particles suitable for CNTs growth. The Fe/MgO catalyst is prepared in situ in a hot zone of the fluidized bed reactor and the CNTs on the catalyst are continuously produced.

2. Experimental procedure

Fig. 1 shows the system used for synthesis of CNTs. The system has three main parts including continuous injection of ferrocene, introduction of MgO particles which are then fluidized by methane and the fluidized bed reactor.

The ferrocene injection system included a tube packed with 60–100 mesh ferrocene particles, through which 60–120 sccm argon was flowing. The tube was located in a constant and uniform temperature bath at 150 °C. The ferrocene injection system is placed on top of the fluidized bed reactor and ferrocene is injected in the hot zone (~700 °C) of the reactor, through an extended tube. An air cooling system was used to prevent overheating of the ferrocene in the tube to temperatures higher than 400 °C. At temperatures higher than 460 °C ferrocene decomposition becomes significant. To enhance the contact of ferrocene and MgO particles in the reactor, a larger diameter (annular) tube covering both the ferrocene injection tube and the fluidized MgO introduction tube, was used for most of the experiments.

1 μm MgO powder (Merck) was pressed and sized to 150 μm average diameter particles and continuously introduced to a fluidization chamber through a star valve at a rate of about

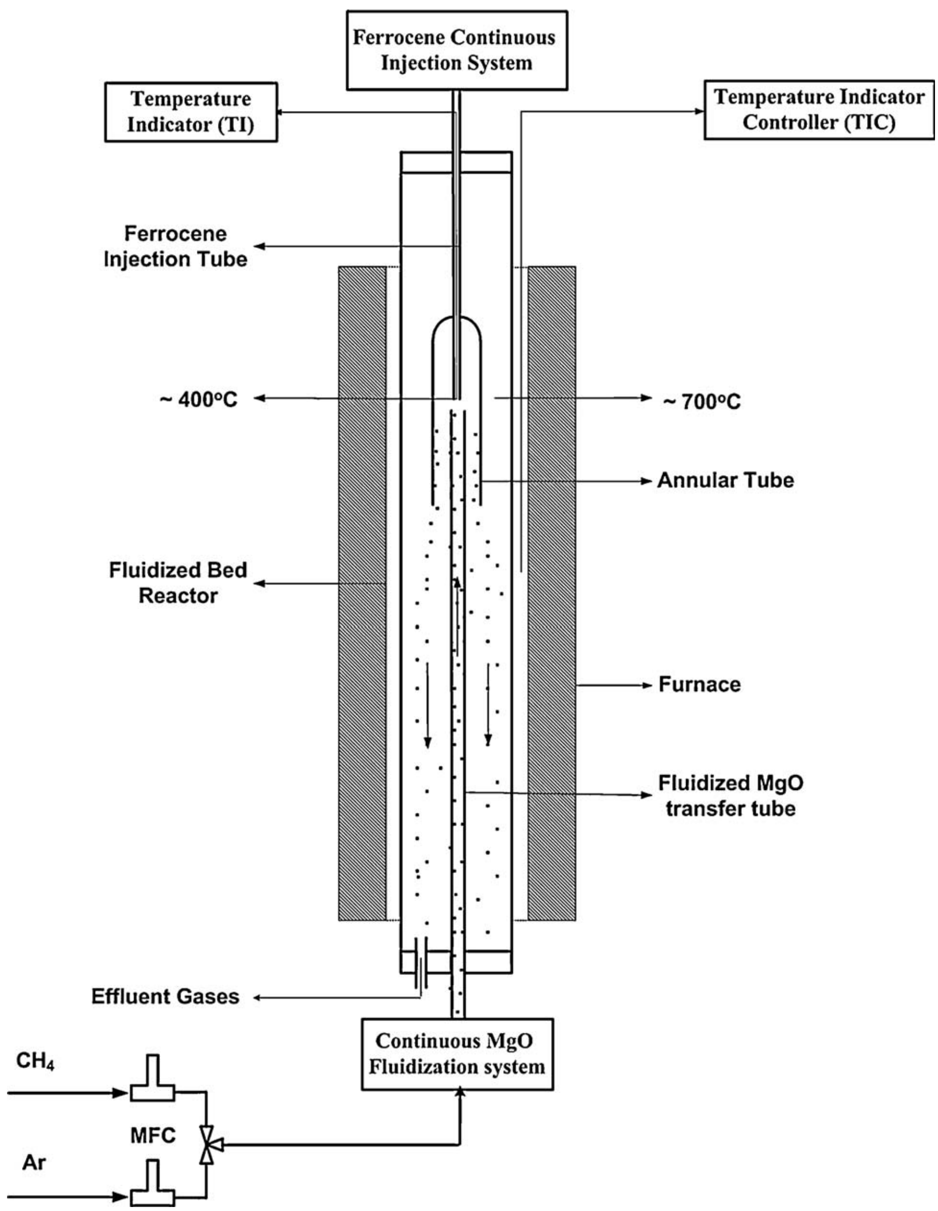

Fig. 1. Schematic diagram of the continuous fluidized bed system used for CNTs synthesis.

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