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Parametric study on vapor-solid-solid growth mechanism of multiwalled carbon nanotubes

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HIGHLIGHTS

- Vapor–solid–solid growth mechanism of MWCNTs was studied in a vertical FBCVD reactor.
- MWCNTs were grown over Al2O3 supported nano-iron buds at very low activation energy.
- FBCVD reactor was operated at temperatures well below the iron-carbon eutectic point.
- Ideally graphitized structures were obtained at a process temperature of 800 °C.
- Tube diameter revealed a narrow distribution of 20–25 nm at the optimum temperature.

GRAPHICAL ABSTRACT

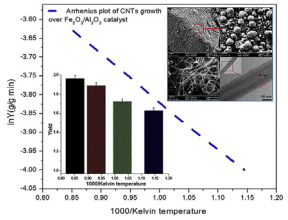

Figure: Arrhenius plot of relatively pure MWCNTs grown over Al_2O_3 supported nano-iron buds

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ABSTRACT

This study aimed at investigating the effect of the fluidized bed chemical vapor deposition (FBCVD) process parameters on growth mechanism, morphology and purity of the multiwalled carbon nanotubes (MWCNTs). Nanotubes were produced in a vertical FBCVD reactor by catalytic decomposition of ethylene over Al_2O_3 supported nano-iron catalyst buds at different flow rates. FESEM, TEM, Raman spectroscopy and TGA thermograms were used to elaborate the growth parameters of the as grown MWCNTs. As the growth process was driven by the process temperatures well below the iron-carbon eutectic temperature (1147 °C), the appearance of graphite platelets from the crystallographic faces of the catalyst particles suggested a solid form of the catalyst during CNT nucleation. A vapor-solid-solid (VSS) growth mechanism was predicted for nucleation of MWCNTs with very low activation energy. The nanotubes grown at optimized temperature and ethylene flow rate posed high graphitic symmetry, purity, narrow diameter distribution and shorter inter-layer spacing. In Raman and TGA analyses, small I_D/I_G ratio and residual mass revealed negligible ratios of structural defects and amorphous carbon in the product. However, several structural defects and impurity elements were spotted in the nanotubes grown under unoptimized process parameters.

1. Introduction

Since their discovery, CNTs have been extensively researched for

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an array of promising physical and chemical properties, such as high mechanical strength, electrical conductivity, chemical stability and specific surface area [1]. Based on specific nature of each application, CNTs are being produced through a range of growth processes including electric arc discharges, laser ablation, chemical vapor deposition (CVD), etc [2]. Although the first two processes are capable of producing CNTs with high degree of crystallinity at a process temperature of 3000 °C or above, the production cost of such processes is considerably high. In these processes, higher input energies are needed to maintain such a high temperature [3]. Additionally, such processes are carried out under vacuum or very low pressures and therefore their expansion to large scale production is not a trivial case. A survey of past literature has shown CVD as a best practice for unequivocal results on structural growth of nanotubes as compared to other available methods [1-4]. The anticipated benefits of CVD technique include flexible geometry, relatively low process temperatures, good control over growth parameters and low production cost [2,3].

Based on the catalyst handing methods, the available CVD reactors are classified into two distinct geometries, namely horizontal furnace CVD reactors and vertical furnace CVD reactors, as illustrated in Fig. 1. In a horizontal CVD reactor, a quartz boat containing the catalyst is placed in low temperature zone of the horizontally aligned furnace while the substrate is placed in high temperature zone for nucleation of nanotubes. Normally, higher process temperatures are required for vaporization of the metal catalyst, decomposition of the carbon precursor over catalyst particles and finally the initiation of CNTs growth in the low temperature zone of the quartz tube. However, the carbon precursor may not make good contact with the catalyst particles in the boat, which is a precondition for production of high %yield of well-structured nanotubes. Zeng et al. [4] revealed that the carbon yield can be increased by introducing a 2nd boat containing the same amount of the catalyst as the first one and doubling the precursor-catalyst contact area under the same operating conditions. See et al. [5] also reported better carbon yield from a horizontal CVD process with an increase in precursor-catalyst contact area, Nevertheless, the particles of the powder catalyst residing at the bottom of the quartz boat do not make good contact with the carbon precursor and therefore face diffusion limitations. Thereby, the overall catalytic activity of the catalyst particles decreases, consequently the product yield and quality.

It has been reported that, the structural characteristics of CNTs are extremely sensitive to the reactor geometry, process conditions, nature of the carbon source, concentration of the reactants, catalyst activity, precursor flow rate, growth temperature and activation energy [4-6]. The earlier discussed factors reveal limited applications of the horizontal CVD reactors, especially in the case of large-scale production of freestanding nanotubes. The stated discrepancies can be overcome by introducing a vertical quartz tube in the reactor geometry and fluidizing the catalyst particles with bottom-up gas flow [6]. In a fluidized bed CVD reactor (FBCVD), vigorous mixing of the catalyst particles with the carbon precursor is possible under appropriate bed conditions, such as process temperature, reaction time and bottom-up gas flow rate. The catalyst fluidization eliminates the diffusion limitations and provides wide reactive surface area for cracking of the hydrocarbons over the catalyst surface for CNTs nucleation. In line with this, FBCVD reactors are known for high mass and energy transfer rates, which are essentially required to attain highest carbon yield, product homogeneity, catalyst efficiency and selectivity in the nanotubes at the cost of low activation energies [7]. Conclusively, a vertical fluidized bed CVD reactor is a better choice to achieve high tube crystallinity and %yield under the same operating conditions, as defined for a horizontal CVD reactor.

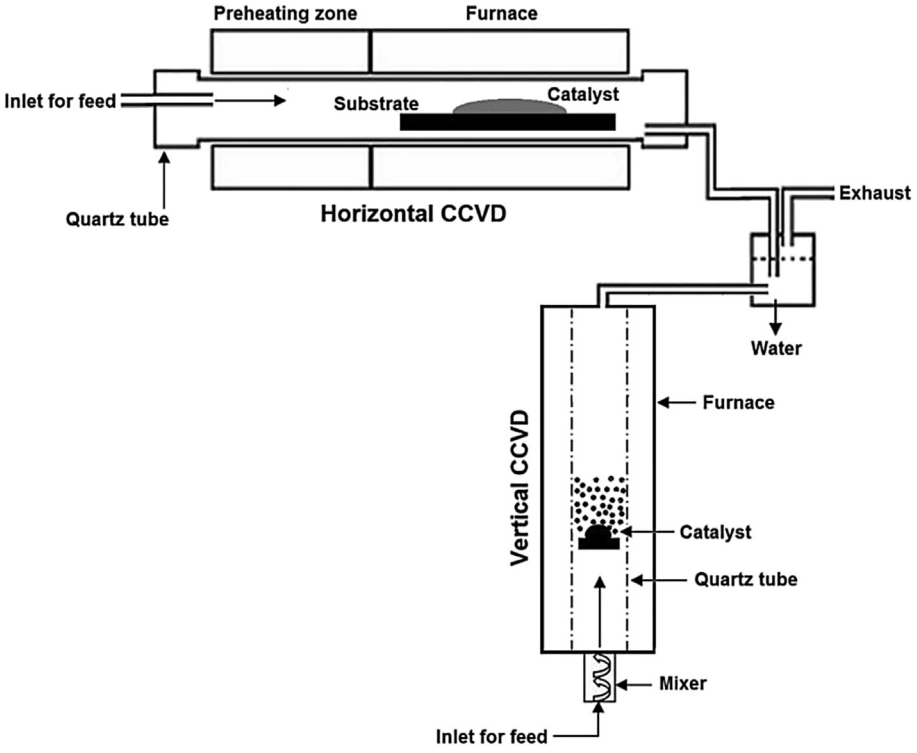

Fig. 1. Geometric illustration of horizontal and vertical furnace CVD processes.