UNIVERSITI PUTRA MALAYSIA

FLUIDIZED BED CHEMICAL VAPOR DEPOSITION SYNTHESIS OF CARBON NANOTUBES AND ITS APPLICATION FOR CELLULASE IMMOBILIZATION

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By

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Chair: Professor Fakhru'l-Razi Ahmadun, PhD

Faculty: Engineering

Over the past decade, Carbon Nanotubes (CNTs) have evolved into one of the most important material under investigation, as they can be used in various applications, due to their excellent unique characteristics. If the CNTs are ever to fulfill their promise as an engineering material, commercial production will be required. Recent advances on Chemical Vapor Deposition (CVD) synthesis of CNTs have shown that fluidized bed reactors have a great potential for commercial production of this valuable material. However, Fluidized Bed Chemical Vapor Deposition (FBCVD) is still in its infancy and further studies and innovations are needed.

Accordingly, the first objective of this study was to develop a FBCVD process for the synthesis of CNT using ethanol (as a carbon source) in the presence of iron and cobalt catalysts supported on alumina. At this stage, attempts were made to find the best value for ethanol flow rate and amount of catalytic particles. The second objective was to investigate the inherent characteristics of catalytic particles, namely, composition and particle size range on FBCVD synthesis of CNT. The maximum carbon deposition efficiency obtained from the experiments was 85%. The deposited carbon was estimated to contain CNTs with a purity of approximately 98% based on thermogravimetric analysis. This result was achieved when 5 g catalytic particles comprising iron: cobalt, with weight percentage of 2:1% and particles size of 10-20 μm were fed into the reactor and the operating parameters including ethanol flow rate, temperature and time of the reaction were set at 2 Sccm, 600 ºC and 30 min, respectively.

In addition to the FBCVD synthesis of CNTs, the possibility of cellulase immobilization on carriers consist of CNT was investigated. A circular-shaped flake nanocomposite made of chitosan-CNTs with a uniform diameter of about 4 mm was fabricated and examined for cellulase immobilization. Physical adsorption of cellulase on carriers composed of chitosan-CNTs revealed that the activity of the immobilized cellulase on the chitosan-CNTs supports is about 3.25 U/g, which is fairly higher than the activity of the immobilized enzyme on the pure chitosan carriers (~ 2 U/g). The activity of the immobilized cellulase on chitosan-CNT carriers was estimated approximately 65% of the free cellulase activity (5.4 U/g), while it was only 40% for enzyme immobilized on pure chitosan supports. Moreover, the immobilized cellulase on the chitosan-CNTs carriers had almost 70% of the fresh

enzyme activity after using it three times. They also retained about 85% of the initial activity after two weeks storage at 4 ºC.

In this dissertation, a selective FBCVD process for gram scale production of CNT was developed. Besides that, it was shown that the characteristics of the catalytic particles, composition and particle size range, have significant impacts not only on the process efficiency but also on the product selectivity and its morphology. In further attempts, the feasibility of using CNT for cellulase immobilization was investigated. Results indicated significant improvement on the physical adsorption of cellulase when the carriers composed of CNT was used. The enzyme reusability and storage ability were also improved when CNT was present in the carriers.

Abstrak tesis yang dikemukakan kepada Senat Universii Putra Malaysia sebagai memenuhi keperluan ijazah Doktor Falsafah

TURUS TERBENDALIR PEMENDAPAN WAP KIMIA SINTESIS KARBON NANO TIUB DAN UNTUK APLIKASI IMOBILISI SELLULASE

Oleh

FIROOZEH DANAFAR

Disember 2010

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Penyelidikan berkenaan karbon tiub nano (CNT) telah berkembang sejak sedekad lalu sehingga menjadi antara penyelidikan utama disebabkan oleh ciri-cirinya yang unik yang sesuai untuk pelbagai aplikasi. Untuk menjadikannya sebagai bahan kejuruteraan, penghasilannya dalam jumlah komersil adalah sangat perlu. Kemajuan terkini dalam sintesis CNT melalui kaedah pemendapan wap kimia (CVD) menunjukkan bahawa turus terbendalir mempunyai potensi yang besar dalam menghasilkan CNT pada skala komersil. Walaubagaimanapun turus terbendalir pemendapan wap kimia (FBCVD) masih lagi baru dan memerlukan kajian dan inovasi yang mendalam.

Dalam usaha untuk membina kaedah yang tidak mahal dan berkesan untuk pengeluaran besaran CNT, satu proses telah di rekabentuk berdasarkan FBCVD menggunakan methanol dan pemangkin yang mempunyai komposisi besi-kobalt disokong alumina. Hasilnya CNT terhasil dalam kuantiti gram dan bebas dari karbon amorf. Rekabentuk baru ini juga mempunyai pelbagai kelebihan seperti ringkas, murah, kebolehkawalan, dan mudah di skala besarkan menyebabkan ianya sesuai untuk pengeluaran skala komersil.

Lanjutan itu, kesan keadaan zarah pemangkin keatas FBCVD terutamanya komposisi logam dan size zarah telah dikaji menggunakan perlbagai teknik. Hasil menunjukkan bahawa julat size zarah pemangkin dan strukturnya mempunyai kesan yang besar kepada keberkesanan FBCVD. Oleh itu, sifat zarah pemangkin, seperti struktur dan saiz liang, dan taburan zarah nano logam perlu diubah untuk mendapatkan kualiti dan kuantiti CNT yang dikehendaki. Selepas mengambil kira semua hasil, CNT dihasilkan daripada 2 Sccm etanol dialirkan ke atas 5 g zarah pemangkin mengandungi 1-2 peratus berat besi-kobalt dan size zarah dibawah 20 μm, pada suhu 600 ºC selama 30 minit. Dalam keadaan tersebut keberkesanan proses ialah 85% dari segi karbon terhasil yang mengandungi 98% CNT.

Lanjutan kepada sinthesis CNT dalam FBCVD, aplikasi CNT yang terhasil dalam bidang bioteknologi telah diselidik. Secara ringkas, empingan komposit nano terdiri daripada chitosan dan CNT telah dihasilkan dan diselidik untuk aplikasi imobilasi selulase. Selulase memangkin dalam penghasilan pelbagai polimer asli yang mengandungi selulosa. Enzim ini mempunyai pelbagai aplikasi komersil seperti ubahsuai fabrik, kertas dan pulpa, makanan, dan industri farmaseutikal. Lebih dari

itu, wujud potensi yang besar dalam bidang pengeluaran bahanapi bio daripada sisa biomass. Penjerapan fizikal selulase oleh empingan Chitosan-CNT menunjukkan peningkatan dalam kitar semula enzim dan kemampuan penyimpanan enzim berbanding dengan Chitosan asli. Hasil menunjukkan immobilisasi selulase menggunakan empingan Chitosan-CNT masih mampu menghasilkan 70% aktiviti dari kadar aktiviti permulaan enzim selepas digunakan sebanyak tiga kali. Ia juga masih menunjukkan 85% kadar aktiviti selepas disimpan dua minggu pada suhu 4ºC.

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I certify that a Thesis Examination Committee has met on 3 December 2011 to conduct the final examination of Firoozeh Danafar on her PhD thesis entitled "Fluidized Bed Chemical Vapor Deposition Synthesis of Carbon Nanotubes and its Application for Cellulase Immobilization" in accordance with the Universities and University College Act 1971 and Constitution of the Universiti Putra Malaysia [P.U.(A)106] 15 March 1998. The committee recommends that the student be awarded the Doctor of Philosophy.

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not concurrently submitted for any other degree at Universiti Putra Malaysia or at any other institution.

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FIROOZEH DANAFAR

Date: 3 December 2010

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