Development A Method For Production Of Carbon Nanotubes

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Abstract

In this work chemical vapor deposition method (CVD) for the production of carbon nanotubes (CNTs) have been improved by the addition of S. Steel mesh container (SSMC) inside which the catalyst (Fe/Al_2O_3) was placed. Scanning electron microscopy (SEM) investigation method used to study nanotubes produced, showed that high yield of two types of (CNTs) obtained, single wall carbon nanotube (SWCNTs) with diameter and length of less than 50nm and several micrometers respectively and nanocoil tubes with a diameter and length of less than 100nm and several micrometers respectively. The chemical analysis of (CNTs) reveals that the main component is carbon (94%) and a little amount of Al (0.32%), Fe (2.22%) the reminder is oxygen. It was also found that the use of (SSMC) leads to increase in yield by a factor of 3 of (SWNTs) and produces nanocoil at the same time.

Keywords: Carbon Nanotubes (CNTs), Chemical Vapor Deposition (CVD), Stainless Steel Container (SSMC), Catalyst, C_2H_2.

تطوير طريقة لانتاج أنابيب النانو كاربون

الخلاصة

تم في هذا البحث تطوير طريقة الترسيب الكهربائي الكيمياوي (CVD) لإنتاج انابيب النانوكاربون عن طريق إضافة حاوية شبكية مصنوعة من الحديد المقاوم للصدأ (SSMC) والتي تم وضع العامل المساعد (Fe/Al_2O_3) في داخلها. تم أيضا استخدام تقنية المايكروسوب الماسح الالكتروني (SEM) للتعرف وتشخيص نوعين من انابيب الكاربون المنتجة في هذا العمل وهي كما يلي أحادية الجدار(SWNTs) وبقطر وطول اقل من 50 نانوميتر وبضعة مايكروميترات بالتتابع وانابيب الكاربون النانوية الحلزونية وبقطر اقل من 100 نانوميتر وبطول بضع مايكروميترات. واظهر التحليل الكيمياوي لانابيب الكاربون النانوية المنتجة ان مكوناته الأساسية هي الكاربون (94% كار بون) و (0,32%) الألمنيوم و(2,22%) حديد والمتبقي هو الأوكسجين. وجد ان الحاوية المستخدمة (SSMC) ادت الى زيادة الحصيلة بزيادة مقدارها 3 مرات من انابيب الكاربون النانوية وكذلك إنتاج انابيب نانو كاربون الحلزونية في نفس الوقت.

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Introduction

Since the discovery of carbon nanotube in 1992(Iijima, 1991), an intensive research activity has been going on to improve methods and conditions, quality and productivity of carbon nanotubes (CNTs) (Zheng and Liu, 2000; Zeng et al., 2002) reaching rewarding conclusions. Due to their high strength, stiffness, and electrical conductivity, carbon nanotubes are designated as one of the most attractive materials for reinforcing the material in composite and nanoelectronic applications (Calvert, 1992; Mintmire et al., 1992; Hamada et al, 1992; Journet and Bernier, 1994). Among many methods of production (CNTs), the chemical vapor deposition (CVD) method is considered the most promising carbon nanotube production method in terms of industrial production (Tapas et al., 2005; Cinar and ruda, 2006). In principle chemical vapor deposition is achieved by the decomposition of hydrocarbon in the gas phase. Commonly used gaseous carbon sources include methane, carbon monoxide and acetylene with the aid of supported transition metal catalyst, (Ni, Fe, Mo, or Co). The (CVD) method is essentially a two - step process consisting of a catalyst preparation step followed by the actual synthesis of the (CNTs). The selection of a metallic catalyst may affect the growth and morphology of the nanotube. In the last few decades, different techniques have been developed for the carbon nanotube synthesis with (CVD).

Most of research has been focused on improving the catalytic technique itself. Accordingly the main objective of the present work is to develop the method of production of (CNTs) by using (CVD) techniques, and the products are identified by different identification techniques: Optical, scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

Experimental

The experimental setup of (CVD) reactor which was used for fabrication of (CNTs) in this work is shown schematically in figure (1). The reactor consists of tubular furnace (a) in which quartz tube (b) of 900mm in length and (30) mm in diameter is placed horizontally in the tube furnace. Argon gas supplied from cylinder (C) is used as an inert gas. The hydrocarbon gas C_2H_2 is supplied by a cylinder (d) is used as a source of pyrolysis gas. In order to control the temperature microprocessor controller (e) is used.

Preparation Of Catalyst

(6%) of Fe_2O_3 was blended with (10%) solution of novalac in (90) ml of ethanol. Then a thin film of previous blended mixture was painted on alumina substrate. The substrate was dried in oven at $(400)^0C$ for one hour. Ten pieces of substrate of (10) mm length and (5) mm diameter were placed inside a cylindrical shape S. Steel mesh container (SSMC) of (200) mm length and (20) mm in diameter. The (SSMC) was then placed inside the quartz tube furnace.

PREPARATION OF (Cnts)

A catalytic growth of (CNTs) was carried out by the decomposition of acetylene C_2H_2 at temperature $(700)^0C$ for o.5h by introducing a mixture of (C_2H_2/Ar) (50ml/500ml) into the reactor. Finally, the gas flow was switched back to Ar and the furnace was allowed to cool to room temperature before exposing the product to the air.

Samples of (CNTs) were allowed to grow without (SSMC) so that the effect of (SSMC) on the yield of (CNTs) would be investigated. The (CNTs) yield (y) was roughly calculated as follows eq. (1):

$$y(mg/mg) = \frac{C_0(mg)}{B(mg)} \quad (1)$$

Where (C_0) is the weight of as prepared product sample mg and (B) is the weight of the catalyst precursor Fe_2O_3/Al_2O_3 mg.

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Characterization

Scanning Electron Microscopy (SEM)

A Carl Zeiss-Supra with accelerator voltage 5KV (UKM Malaysia) was A Carl Zeiss-supra with accelerator voltage 5 Kv (UKM Malaysia) was employed to observe the structure of carbon nantube. (XRD) pataren of CNTS was record using Standard Phillips type PW1877 Automated powder diffractometer was used with Cu-Kα radiation and a pure Silicon powder as a standard employed to observe the structure of carbon nanotubes.

Results And Discussion

Two type of experiments were carried out, the first with fixed flow rate of Argon fixed as a carrier gas using different reaction temperatures, fixed reaction time and substrate enclosed in (SSMC) container. In the second experiment (SSMC) was eliminated, fixed reaction time and optimum temperature was obtained from the first set of experiment in which a high yield of (CNTs) was obtained for the first set of experiments with Ar fixed as carrier gas. The total amount of (CNTs) deposited on the catalyst after reaction was determined by weight gain in the tube in furnace during the reaction. The influence of the reaction temperature on (CNTs) yield with and without (SSMC) is shown in figure (2). It can be observed that the yield of (CNTs) produced at 400^0C is very low, with the increase in reaction temperature, the yield is increased rapidly, but when the reaction temperature is increased to 700 ^0C, the yield begins to decrease. This may due to the fixed flow rate of argon gas which may cause the oxidation some of the produced (CNTs) after 700^0C and converted to CO_2.

Similar behavior was obtained without using (SSMC) but with a lower yield. The yield gain is increased by a factor of 3 when (SSMC) is used. The (SEM) results are shown is figures (3-6). It is well known that it is difficult to decide from diameters measured by SEM whether a nanotube is single wall or not (Tapas et al., 2005; Cinar and ruda, 2006). It is only used to estimate the tube diameter. Our observation suggest that the product is (SWNTs) rather than (MWNTs). The carbon nanotubs shown in scanning electron microscopy (SEM and TEM) images shown in figures (3-6) were synthesized at high yield in two types:

Single wall nanocarbon tubes with characteristic diameter (20- 40 nm) and nanocarbon coils. The diameter and length of (SWNTs) are less than 50nm and several micrometers, respectively, while the nanocoil diameter and length are less than 100nm and several micrometers respectively.

Our observation suggests that the (SWNTs) grow as a result of using (Fe/Al_2O_3) catalyst while nanocoil is identified when (SSMC) was used. Accordingly the use of (SSMC) leads to increase in yield of (SWNTs) and produces a nanocoil at the same time. The high yield observed when using (SSMC) may be attributed to the effect of (SSMC) on slowing down the velocity of C_2H_2 gas, which may give more chance to gas to decompose in high yield through the tube reactor. Moreover the (SSMC), a stainless steel type 316L consists of different elements Cr(16-18%), Ni (10-19%), Mn (2%), Si (1%) and other traces elements (P,S,C). These elements are deoxidized by carbon and hydrogen of C_2H_2 at high temperature 700^0C and then they may absorb carbon to form crystalline Fe-Cr-Ni-Mn carbide compounds. On which a nanocoils form crystalline compounds.

The spectrum in Figure (7) represent the chemical analysis of the (CNTS) sample obtained by electron diffraction spectroscopy (SDS) of SEM system showing the majority are carbon (94%) and a little amount of Al (0.32%) and Fe (2.22%) and the remainder is oxygen formed (3.33%). Figure (8) shows the (XRD) spectra of (Fe/SSMC) catalyst.

Many peaks observed which may be attributed to graphite and Fe these peaks may be corresponding to the formation of metal carbides. This suggestion agrees well with conclusion drawn by (Kenji et.al, 2004) based on similar observation.

Conclusion

The (CVD) method of production of (CNTs) has been improved by adding (SSMC). The (SSMC) is responsible for high yield production of (CNTs). (SSMC) may also be responsible for growth of carbon nanocoil, in this case we believe that Iron is oxidized and catalyst form nanoparticles by heating to a growth temperature of 700 ^{o}C in Ar atomosphere. The nano particles contain nanocrystal of Iron oxide and other element oxides, suppling of C_2H_2 gas may deoxidize the catalyst and then carbon atoms be incorporated into the catalyst form crystalline carbide compounds, carbon nanocoils may be grown form these crystalline compounds.

Symbols list

B: the weight of the catalyst precursor Fe_2O_3/Al_2O_3 mg.
C_0: the weight of as prepared product sample.
CVD: Chemical Vapor Deposition Method.
CNTs: Carbon Nanotubes.
SEM: Scanning Electron Microscopy.
SSMC: Stainless Steel Mesh Container
SWCNTs: Single Wall Carbon Nanotube.
SDS: Electron Diffraction Spectroscopy.

TEM: Transmission Electron Microscopy.

Y: yield.

References

Calvert, P. Strength in Disunity. Nature, 357: 365, (1992).

Cinar, O. and ruda, y. Carbon Nanotube Synthesis via the Catalytic CDV Method, Areview on the Effect of Reaction Parameters. Fullerenes, Nanotubes, and Carbon Nano structures, 14: 17-37, (2006).

Hamada, N., Sawada, S., and Oshiyama, A. "New One – Dimensional Conductors: Graphitic Microtubules". Phys. Rev. Lett., 68: 1579, (1992).

Iijima, S. "Helical Microstructure of Graphitic Carbon Nature", 354: 56, (1991).

Journet, C. and Bernier, P. "Production of Carbon Nanotubes". Appl. Phys. A, 67: 1, (1994).

Kenji, N, Lujun, P. and Yoshikazu, N., "In Situ Study of Fe/ITO Catalysts for Carbon Nanocoil Growth by X-ray Diffraction Analysis". Japanese J. of Appl. Phys. A, 8:43, pp 5665-5666. (2004).

Mintmire, J. W., Dunlap, B. L., and White, C.T. are Fullerene Tubules Metallic. Phys. Rev. Lett, 68: 631, (1992).

Tapas L., Kertesz K., Vertesy Z., Horvath Z. E., Koos A. A, Z.Osvath, ZS. Sarkozi, Al. Darbont, L. P. Biro., "Diameter and Morphology Dependence on Experimental Conditions of Carbon Nanotube Array Arown by Spray Pyrolysis"Carbon 43 970- 977, (2005).

Zeng, X., Cheng, G., Yan, X., and Xu, "Production of Multi- Wall Carbon Nanotubes on a Large Scale". Physical B, 323: 330, (2002).

Zheng S. and Liu J. "A scalable CVD Method for The Synthesis of Single – Walled Carbon Nanotubes with High Catalyst Productivity". Chem. Phys. Lett., 322: 321, (2000).

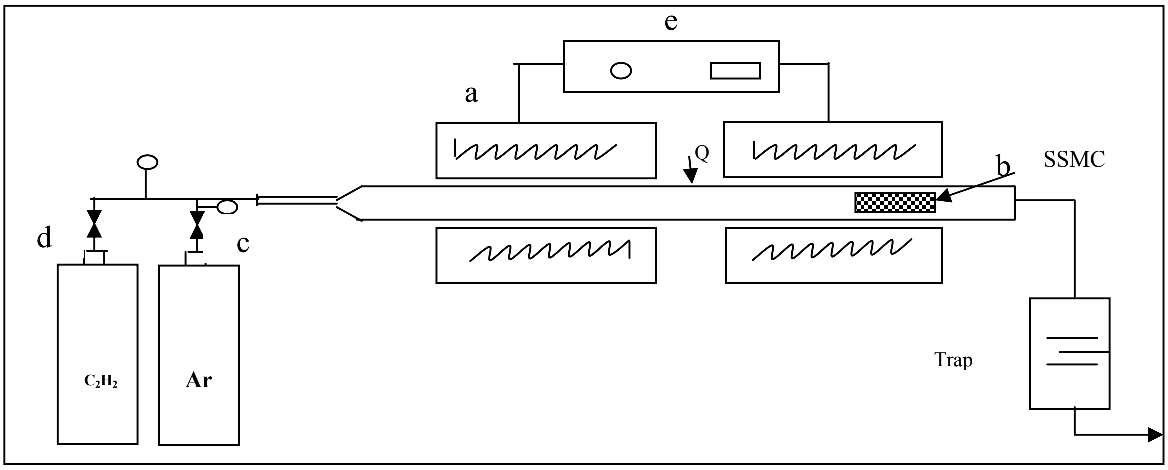


Fig.1: (CVD) Experimental Setup: (a) Tubular Furnace (b) Quartz tube (c) Argon Gas Cylinder (d) Acetylene Gas Cylinder (e) Furnace Controller

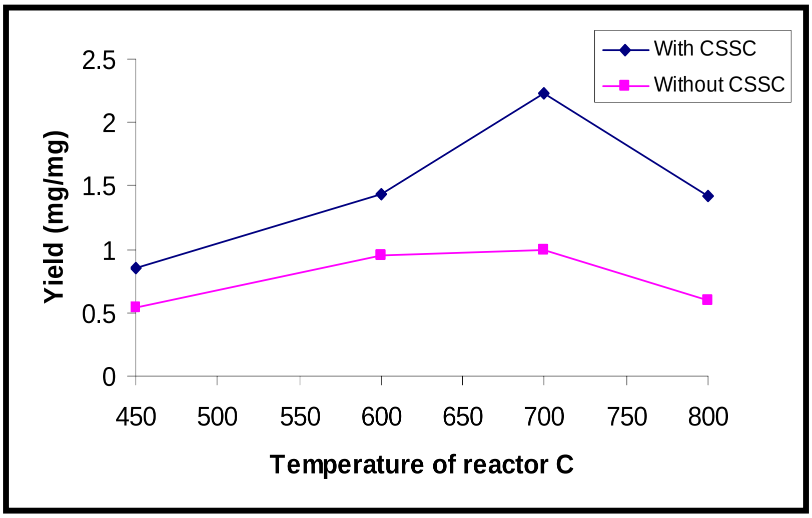
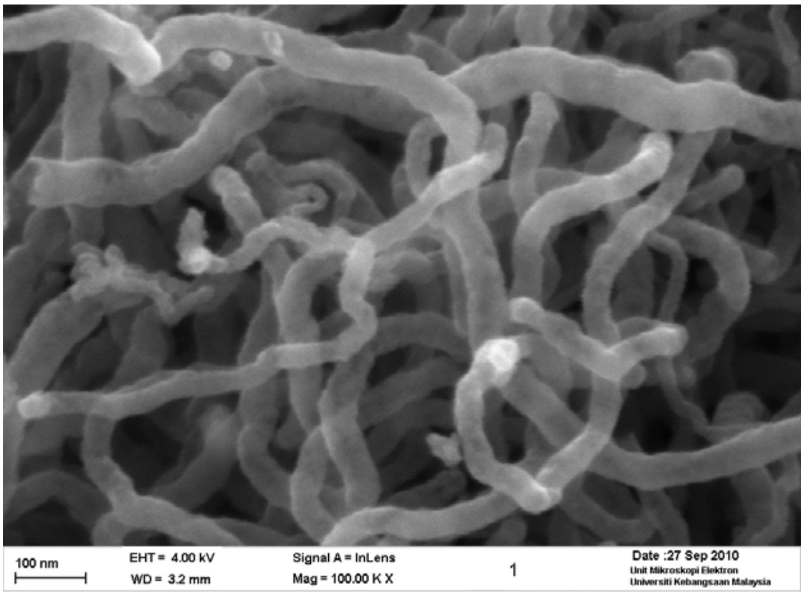


Fig.2: Effect on Reaction Temperature on the Yield of (CNTs)

a: with



(SSMC), b: without (SSMC)

Fig.3: SEM Image of (SWCNTs)

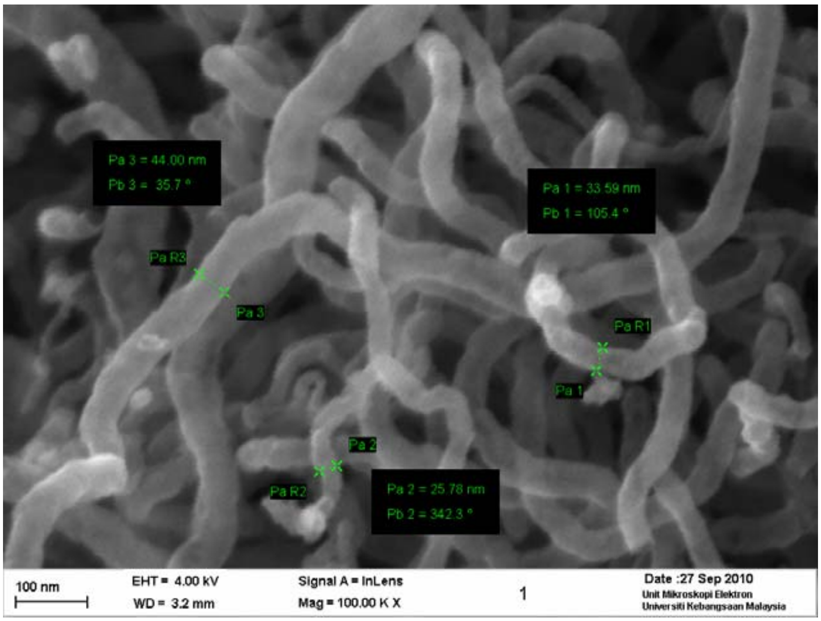
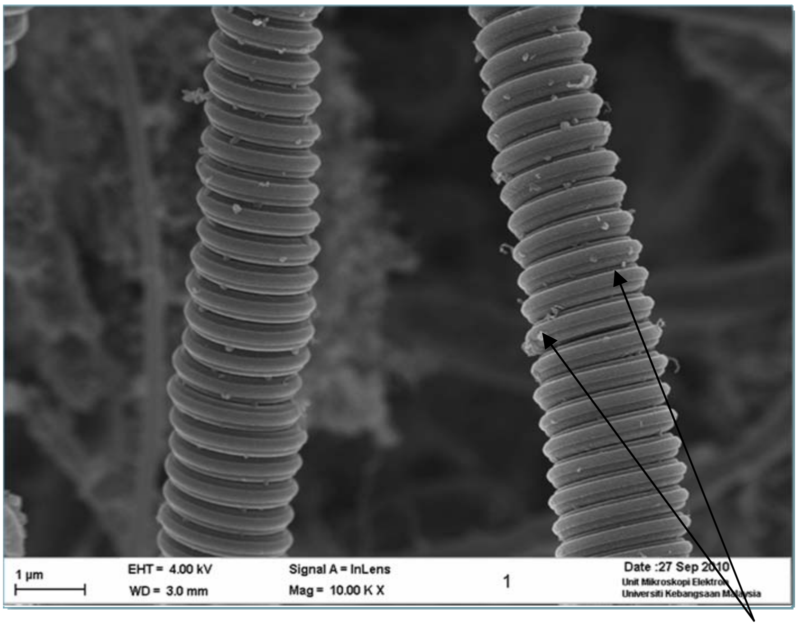


Fig. 4: SEM Image of (SWCNTs)

Fig.5: TEM image of (SWNTs)



Impurities (catalyst)

Fig.6: SEM Image of Nanocoil

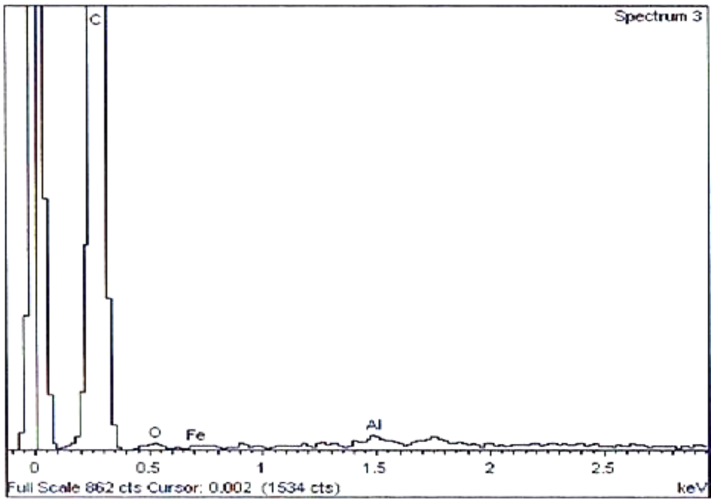


Fig.7: Chemical Analysis of (CNTs)

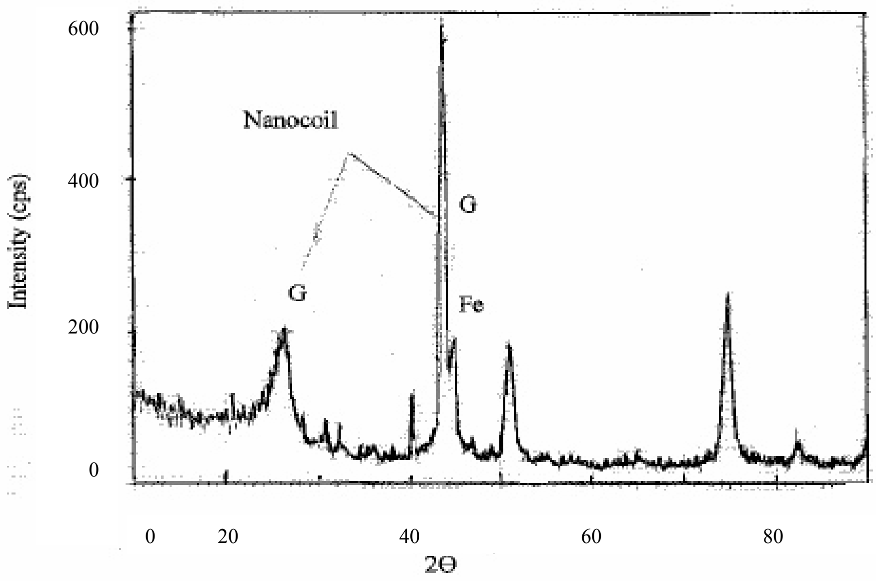


Fig.8: XRD of (SSMC) after Heated at 700°C in (CVD) Reactor