Synthesis of Multi-Walled Carbon Nanotubes from Iraqi Natural Gas/CO Mixture by Catalytic Flame Fragments Deposition Method

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Multi-walled carbon nanotubes (MWNTs) were synthesized from Iraqis natural gas using flame under carbon monoxide atmosphere. The study focuses on abilities to synthesis and characterization of carbon nanotubes (CNTs) using simple, easy, low cost by natural material. The reactor has been designed for synthesis of carbon nanotubes CNTs from natural gas which acted as a source of carbon in addition to supplying thermal energy instead of electrical energy. Crystallographic and morphological of CNTs have been characterized using powder X-ray diffraction, Raman spectroscopy, transmission electron microscope and thermal gravimetric analysis. The analysis refers to synthesized MWNTs with purity 57.80 % and outer diameter 6.6-17.9 nm, inner diameter 3.2-6.3 nm which equal to 3-9 of graphene layers while the length of tubes is 0.8 to 2 µm.

Keywords: Multi-walled carbon nanotubes, Natural gas, Reactor homemade, Carbon monoxide.

INTRODUCTION

The urgent need for nanotechnology in the 21th century has led to a growing demand for chemical compounds to achieve advanced technology. Maybe carbon nanotubes (CNTs) represent one of the common nanomaterials that used in huge applications such micro and nanoelectronics devices [1], drug delivery [2] energy and environmental applications [3]. The remarkable physio-chemical properties of CNTs have been foreword multi-use materials and still being tested for many applications. The abilities of CNTs to use in the different application not only for varying types such as SWNTs or MWNTs but a variant on orientations of carbon atoms [4] on graphene sheets. Many literatures [5,6] reported the common routes of synthesis of CNTs such as arc-discharge, laser ablation and chemical vapour deposition.

Flame fragments deposition (FFD) method is one of many techniques used to synthesize carbon nanomaterials which depend on chemical materials as sources of carbon and source of energy for carbon deposition. Flame fragments deposition method [7] use hydrocarbon in gas phase such CH_4 and C_2H_2 reacts with O_2 to produce a gaseous mixture which includes CO_2, H_2O,

CO, H_2 and many species of free radicals. The free radicals [8,9] responsible for producing tubular structures on the upper side of the reactor. The influence of chemical energy [10] for decomposition carbon represented by limitation the carbon deposition with orientation endothermic reactions to build the tubular structure. This capacity is considered the most important characteristic which shows preference compared to the previous methods. Mostly, the flame methods use hydrocarbon gases with high purities which may cause limitation due to all of its use as a source of energy. Natural gases one of the components of crude oil mostly in oil countries which separated during the refining operations and disposed of by burning in refining towers, only a few ratios exploit. Natural gas is mainly mixture of methane, ethane, propane and butane, as well as H_2O, CO_2, N_2 and some sulfur compounds. Awadallah *et al*. [11] synthesized MWNTs from natural gas as a carbon source using the catalytic chemical vapor deposition (CCVD) technique over Ni-Mo and Co-Mo supported on Al_2O_3 catalysts at 700 ºC in a fixed horizontal reactor. According to the review the yield of carbon nanotubes was 55.01 wt% when use Ni-Mo as catalyst and 33.38 wt% for Co-Mo catalysts.

Bonadiman *et al*. [12] used natural gas to synthesize multi-walled carbon nanotubes and single-walled carbon nanotubes by catalytic chemical vapor deposition at 1000 ºC. The process included using MgO as a catalyst support with Fe-Mo/MgO system which obtained by the impregnation to synthesis SWNTs and decomposition system was succeeded in synthesis MWNTs. Bang *et al*. [13] characterized CNTs and fullerene which had been collected in propane and natural gas flame emissions from domestic cooking stoves. Iraqis natural gas mostly consisted of propane and butane. In our present work, the simple and easy method of using the natural product as sources of energy and carbon which represent by flame fragments deposition method and Iraqi natural gas respectively were used to synthesize carbon nanotubes. Precipitation process was subjected in an atmosphere of carbon monoxide gas when forming from the decomposition of methanol alcohol inside the reactor. The product was characterized by X-ray diffraction, Raman spectroscopy, transmission electron microscopy and thermogravimetric analysis.

EXPERIMENTAL

Iraqis natural gas was supplied from local markets, which analysis in petroleum research and development center, on Iraqi. The analyses were performed in winter and Table-1 shows the physical properties of natural gas and percentage volume of natural gas. The H_2O_2 was purchase from Barcelona, Spain in 30 % percent weight. Methanol with purities (99.93 %) was supplied from Alfa, Aesar.

Precipitation unit: Fig. 1 shows the home-made reactor and the experimental setup for the synthesis of carbon nanotubes when achieved the flame. The reactor consists of a chamber with 8 L in capacity, with two laminar in the lower part with two sources of gases. In this case, part 5 refers to the surface of precipitation when decomposition was accrued which covered with aluminum foil. The system was supplied by thermal cable to control the temperature by thermal cable with 30 cm in length and ability to control the temperature until 800 ºC and accuracy ± 2 ºC. The burner nozzle outlet diameter was 2.7 cm, while the body inner tube diameter was 3 cm and height 8 cm. The distances between the sources of combustion and the upper surface were 15 cm. Two mass flow controllers with an accuracy of ± 2.5 % (BROKER, DK800S-3) were used to control the mass flow rate of natural gas and air.

Synthesis of carbon nanotubes: The laminar of methanol start ignition with an excess amount of oxygen for 10 min. The role of methanol was reducing of oxygen in the chamber with produce excess amount of CO as the atmosphere of precipitation with a minimum value of soot and keep the temperature in the lower section of chamber at 150 ºC. After that the laminar of natural gas start to ignition for 20 min with maintaining the methanol laminar working with fixed flaw rate for O_2/natural
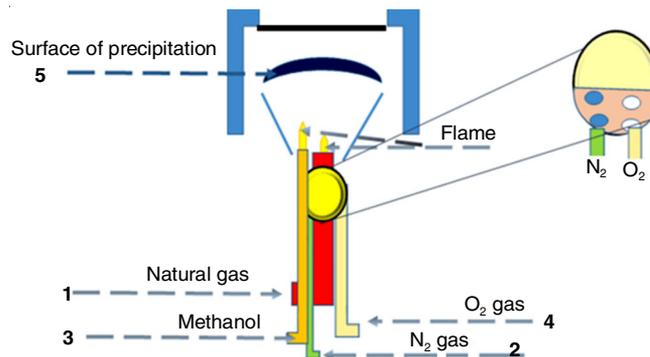

Fig. 1. Schematic diagram of homemade reactor and experimental setup for synthesis carbon nanotubes

(3/1) gas 600 cm^3. After that stopped flow O_2/ natural gas and methanol with the cool chamber to room temperature by the flow of nitrogen gas with flow rate 500 cm^3/min.

Purification process: As-prepared CNTs were purified as we reported in our previous work [14]. Briefly, 125 mg of as-prepared sample was desperation with an ultrasonic water bath in 150 mL ethanol alcohol for 10 min. The complementary of first step includes using separation funnel, to re-distribute the components which form the aggregate particles that removed from the solution. After filtration and drying at 70 ºC, the sample was treated with 150 mL of H_2O_2 at 15 ºC for 12 h with stirring by a magnetic stirrer. The solution allowed to reach for room temperature, then heating gradually to 80 ºC to complete dissociation most of H_2O_2. Finally, the sample was washed with distilled water and dried at 100 ºC for 12 h.

Characterization: X-ray diffraction (XRD) patterns were done on a (RigakuRotalflex) (RU-200B) X-ray diffractometer using CuKα radiation (λ = 0.15405 nm) with a Ni filter. The tube current was 100 mA with a tube voltage of 40 kV. The 2θ angular regions between 10 and 85º were explored at a scan rate of 5º/min with resolution at 0.02º. Raman analysis was performed from 100-3400 cm^{-1} by Sentara infinity 1 Bruker with using laser light at 530 nm, for 5 lops per 2 sec and resolution equal to 3-5 cm. Transmission electron microscopy was done by (Philips CM30 microscope operating at 300 kV) which equipped with a Gatan SS CCD camera and a Digital Micrograph software for the acquisition of electron diffraction patterns. TGA measurements were carried out in Al_2O_3 crucibles in a nitrogen atmosphere at a heating rate of 10 °C/min using a TG 209 F3 Tarsus® instrument (Netzsch, Germany).

RESULTS AND DISCUSSION

X-ray diffraction analysis: Fig. 2 shows two peaks at 25.06º and 43.14º which commonly seen with carbon nanotubes [14]. Mostly, the two peaks can be attributed to the diffraction from C(100) and C(002) planes of the carbon nanotubes, respectively.

TABLE-1
PHYSICAL PROPERTIES AND VOLUMETRIC RATIOS OF IRAQI NATURAL GAS CONTENTS

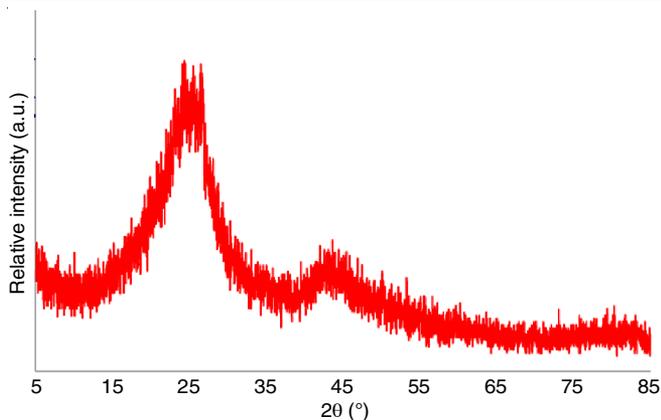| Physical properties	Values	Component	Volumetric ratio (% V max)
Vapour pressure at 37.8 °C	10 kg/cm^2	Ethane	0.6
Heat vapourization 95 %	2.2 °C	Propane	60-70
Density at 15 °C	0.534-0.551 g/cm^3	Butane	30-40
Residual of vapourized 100 mL	0.05 mL	< C5	2.0
		Sulphite content	150 ppm

Fig. 2. X-ray diffraction pattern of synthesized multi-walled carbon nanotube

Raman analysis: Raman spectrum (Fig. 3) showed the main peak which is the D and G bands at 1369 and 1595 cm^{-1}, respectively [15]. The D band is induced to disordered carbon atoms or may relate to sp^3 hybridized of carbon nanotubes. The G band is due to the sp^2 hybridized derived from splitting of E$_{2g}$ stretching mode in sheets of graphite. The distinguishable feature of CNTs was G+D band at 2964 cm^{-1} which appear as weak peak [16,17]. The increased intensity of D band as compared to G band mostly refers to the functional groups which produce during production and purification process with hydrogen peroxide [18]. The law ratios (ID/IG = 0.92); may be related to reducing the intensity of the G band due to the presence of high defects on the walls of tubes. The G and D band observed as wide with semi-equals high due to an amorphous phase and high degree of disorder in the structure of sp^2 hybridized to graphite structure at low-temperature growth [19].
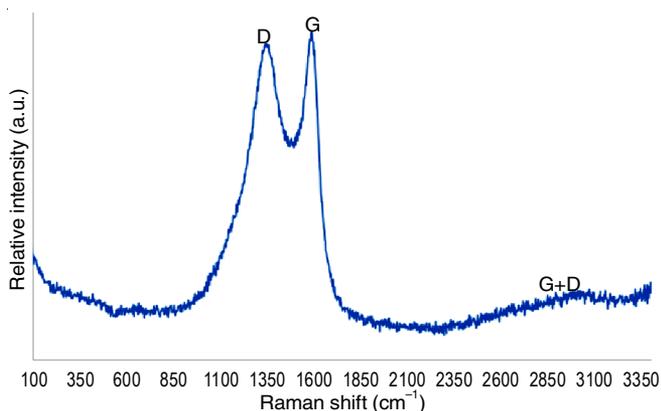

Fig. 3.   Raman spectra of synthesized MWNTs by flame fragments deposition method

TEM analysis: TEM shows the images of as-prepared tubular strictures with many balls which referred to unconverted carbon (Fig. 4). The image shows filaments of carbon nanotubes with diameter arrange between 6.6 to 17.9 nm and the inner diameter of nanotubes between 3.2-6.3 nm with a thickness of wall reach to 11.6 nm. From the inner and external diameter, it can be concluded that the number of graphene layers arranged from 3-9 layers which are mostly MWNTs [20].

Thermal analysis: The thermogram (Fig 5) shows three regions, the first region between 100-425 °C when 2.49 % loss mass due to the evaporation of adsorbed water [21] and decom-
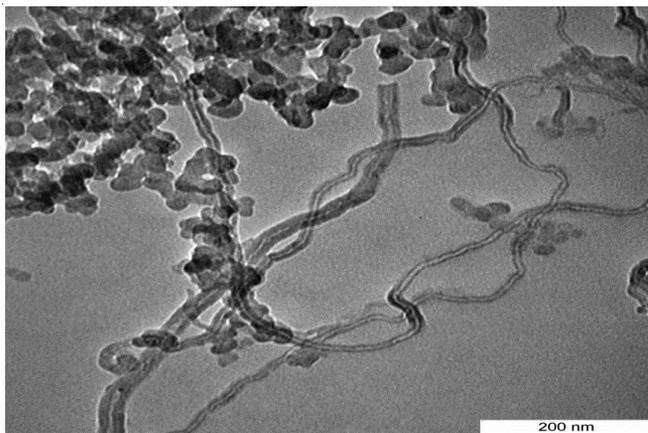

Fig. 4. TEM image of synthesized MWNTs by flame fragments deposition method
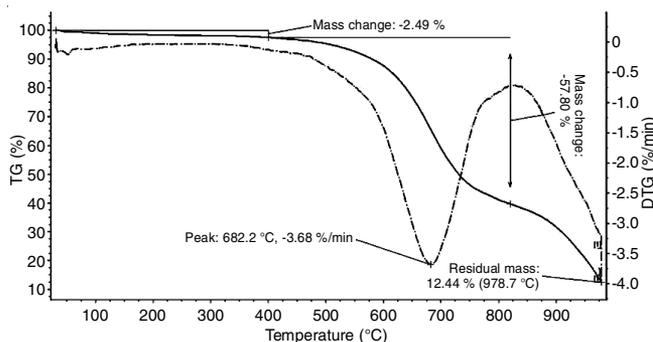

Fig. 5. TGA of synthesized carbon nanotubes after purification

position unconverted carbon [22]. The second part of 425-682 °C witnessed a loss 57.80 % of mass that can be related to decomposition of synthesized CNTs [22,23] with a clear exothermic peak for decomposition of synthesized MWNTs [24]. The residual materials showed 12.44 % due to the remaining support of aluminum compound used in preparation method.

The important of this work can be related to synthesis of MWNTs at low temperature, high production and low cost without catalyst which make the process of purification easier. The role of CO not only as sources to consume the oxygen in the chamber of reaction but as an initiator of carbon to produce tubular structures. The CO atmosphere behaves as donor and catalyzer when the reversible reaction of CO to produce CO$_2$ and carbon [25]. Natural gas as mixture of aliphatic and aromatic hydrocarbons can produce carbon with high concentration [26,27] which catalyzed to precipitate over carbon free radical produced with the decomposition of methanol. Therefore, the precipitation accrued due to inner catalyzer from CO whereas paves the way for the process of carbon deposition without using a transition metal catalyst.

Conclusion

Multi-wall carbon nanotubes successfully synthesized by flame method shows a high efficiency to make precipitation in easy and safety manner without any complication. Flame fragments deposition synthesis has been utilized to produce CNTs from Iraqis natural gas in CO atmosphere at aluminum foil as surfaces of precipitation. Thermogravimetric analysis and TEM images show that the CNT samples contained 57.80 % of MWNTs. The method can be modified to be ideal for

synthesis different types of carbon nanotubes in additions to abilities to make its ideals towards high quantities.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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