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Insitu Synthesis of Multi Walled Carbon Nano Rings by Catalytic Chemical Vapor Deposition Process

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Funding Information:	VB Ceramics Consultancy (G8/83628/2015) — Mr sivamaran venkatesan
Abstract:	Carbon nano rings (CNRs) are found to be the most promising nanostructure for the application of nanoscale devices. The CNRs are synthesized by many post-treatment processes such as ultrasonication, acid treatment. The post treatment process may alter the properties of the rings. Hence, in this investigation, an attempt has been made to synthesize multi-walled carbon nano ring's (MWCNRs) in a single step process (as-synthesized condition itself). The CNRs are synthesized by catalytic chemical vapor deposition (CCVD) process using NiO/Al2O3 as catalyst material and acetylene was used as the precursor gas. FESEM confirms the as-grown ring structure and HRTEM reveals the effect of the isolation process. The rings typically have thickness ranges from 7 to 17 nm and diameter ranges from 10 to 190 nm. Additionally, FTIR, Raman spectroscopy were used to evaluate the functionality and structure of the rings respectively. The scientific justification behind the growth mechanism to the CNRs and open rings was discussed in this paper. The agglomerated morphology of catalyst particles has a significant effect on the growth of ring structure.
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Author Comments:	It is a research paper that deals with synthesis of multi walled carbon nanorings (MWCNRs) by catalytic chemical vapor deposition (CCVD) process and also, we investigated the effect of CCVD process parameters on the growth of multi walled carbon nanorings. The highlight of this paper is demonstrated a schematic representation that briefs the growth of CNRs.
Response to Reviewers:	Reviewer #2: The authors synthesized multi-walled carbon nano ring's in a single step process. FTIR, Raman spectroscopy were used to evaluate the functionality and structures of the rings respectively. There are no any logical errors for the date. However, there are also some suggestions are given for improving the manuscript. The following comments should be addressed.

1. The authors should provide the high-resolution images of SEM.
We have provided FESEM images of Carbon nanoring's (CNRs), resolution starting from 1 micrometer to 100 nm. FESEM analysis was conducted over the carbon samples to confirm the presence of ring structure and 100 nm resolution is found to be enough to confirm the structure that present in the carbon samples. Additionally, we provided HRTEM images with higher magnifications than FESEM images, to evaluate the structure of CNRs.

2. NiO/Al2O3 particles has been synthesized, however, no any evidences could be seen that the successful synthesized of NiO/Al2O3 particles.
EDAX analysis is included in Fig.1b and it confirms the presence of NiO/Al2O3 particles

3. The flow rate of precursor gas has greater influence on the bending nature of nanotubes. The evidences should be provided.
Evidence is provided in Fig.2e, and it shows absence of ring structure. The flow rate of hydrocarbon gas was reduced from 180 ml/min to 140 ml/min, to study the effect of the flow rate of precursor gas on the bending nature of nanotubes.

4. The English level should be improved.
The entire manuscript was read thoroughly and carefully and changes were made, to improve the quality of the English level of this article.

5. Why the Raman spectra of carbon nano rings and straight nanotubes have such difference?
Carbo nanorings expected to have the largest splitting spectra due to both the Zone-folding effect and the curvature effect (Jorio et al. 2000, Physical Review Letters).

Reviewer #3: A research paper with title "Insitu Synthesis of Multi Walled Carbon Nano Rings by Catalytic Chemical Vapor Deposition Process" has been submitted in International Nano Letter. Authors claimed that could synthesize MWCNRs and then some normal characterizations were carried out. A CVD method using NiO/Al2O3 as catalyst was used to grow MWCNRs. Authors should answer following questions before my final decision.

1- Abstract should be included some numerical results.
Yes, Included numerical results in the abstract

2- I found some nonrelated references in the manuscript such as in this sentence "Following CNTs, the single-walled carbon nanoring's (SWCNRs) and multi-walled carbon nanoring's (MWCNRs) are found to be the most interesting carbon nanostructure, since they are considered as the giant of all carbon structure and directly used as a nanoscale device [4]." Ref [4] is not related to nanorings.
They have mentioned as “nanotorus” instead of “nanorings”. Torus mean toroidal structure, toroidal mean circular. Hence, the statement quoted in the introduction is related to the nanorings only.

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4- There are several typing, grammatical, and Ref address such as Ref [9] that does not have correct information. It is Science 293, 1299-1301 (2001).
Yes, Checked and corrected.

5- Quality of Fig 1 is very low.
Yes, checked and included high quality image of Fig.1 (Improved the quality of image by high dpi (Dots per inch))

RESPONSE TO THE COMMENTS RECEIVED FROM INTERNATIONAL NANO LETTERS, SPRINGER

"INSITU SYNTHESIS OF MULTI WALLED CARBON NANO RINGS BY CATALYTIC CHEMICAL VAPOR DEPOSITION PROCESS"

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ABSTRACT

Carbon nano rings (CNRs) are found to be the most promising nanostructure for the application of nanoscale devices. The CNRs are synthesized by many post-treatment processes such as ultrasonication, acid treatment. The post treatment process may alter the properties of the rings. Hence, in this investigation, an attempt has been made to synthesize multi-walled carbon nano ring's (MWCNRs) in a single step process (as-synthesized condition itself). The CNRs are synthesized by catalytic chemical vapor deposition (CCVD) process using NiO/Al_2O_3 as catalyst material and acetylene was used as the precursor gas. FESEM confirms the as-grown ring structure and HRTEM reveals the effect of the isolation process. The rings typically have thickness ranges from 7 to 17 nm and diameter ranges from 10 to 190 nm. Additionally, FTIR, Raman spectroscopy were used to evaluate the functionality and structure of the rings respectively. The scientific justification behind the growth mechanism to the CNRs and open rings was discussed in this paper. The agglomerated morphology of catalyst particles has a significant effect on the growth of ring structure.

Keywords: Carbon nano rings, chemical vapor deposition, Multi walled carbon nanotubes, Growth mechanism

1.0 INTRODUCTION

The field of nanotechnology has grown discernible, because of research that was undertaken in carbon nanotubes (CNTs), especially on synthesizing different allotropes of carbon nanomaterials, like carbon nanoring's [1], carbon nanorods [2], carbon nanosphere [3], etc. Following CNTs, the single-walled carbon nanoring's (SWCNRs) and multi-walled carbon nanoring's (MWCNRs) are found to be the most interesting carbon nanostructure, since they are considered as the giant of all carbon structure and directly used as a nanoscale device [4]. Recently, several research groups have reported on modifying the as synthesized CNTs into the formation of the ring shape carbon tube via post treatment processes [5,6,7]. Mostly, the post-treatment process involves chemical treatment to bend the CNTs into the ring shape, structure, which might alter the essential characteristics of nanotubes [8]. To overcome these problems, it is indeed necessary to synthesize carbon nano rings (CNR) in the as-synthesized condition itself.

CNR can be synthesized by various methods, including laser growth [9], ultra-sonic bath [10], chemical vapor deposition process [8,11]. Compared to other methods, the chemical vapor deposition (CVD) process is capable

of synthesizing CNR in a single step. However, in other processes, first CNTs were synthesized and then tubes were subjected to an acid treatment to form rings [12]. Further, the formation of rings in a chemical process may enhance the essential characteristics of the CNR.

Zhou. et. al, [5], have synthesized Single-Walled Carbon Nanoring's (SWCNRs) in a floating catalyst chemical vapor deposition (FCCVD) process. FCCVD consists of two-furnace setup, where the catalyst was placed in the first furnace and the substrate was placed in the second furnace at 1100 °C. **Song. et. al,** [13], have synthesized SWCNRs in a similar manner using a FCCVD process by ferrocene as a catalyst at 1100 °C. Few researchers only have reported the synthesize of CNR via catalytic CVD [11,14] process. There is a lack of information on the characteristics of the catalyst particles that were used to synthesize CNR, especially in catalytic chemical vapor deposition (CCVD) process.

Recently, **Venkatesan. et. al,** [15], optimized the CCVD parameters to synthesize well-aligned multi-walled carbon nanotubes (MWCNTs) using Ni/Al_2O_3 as a catalyst material. It is believed, that CNT bundles can be grown abundantly using agglomerated catalyst particles. Hence, in this investigation, an attempt has been made to synthesize CNRs via CCVD process using agglomerated NiO/ Al_2O_3 as catalyst and acetylene as a precursor gas.

2.0 EXPERIMENTAL

The NiO/Al_2O_3 catalyst was prepared by impregnation method as proposed by **Kong.et.al,** [16]. The final step of catalyst preparation, fine grinding was avoided to achieve the agglomerated catalyst, to facilitate the formation of rings.

The MWCNTs was synthesized at atmospheric pressure in a quartz tube reactor (Diameter: 70 mm, Length: 300 mm) by thermal chemical vapor deposition machine. The reaction temperature was kept at 900 °C and the acetylene was used as a precursor gas, flow rate was held at 180 ml/min. After a growth period of 25 mins, the as-grown carbon samples were collected to characterize using a different image and analytical techniques. After FESEM analysis, the rings were extracted from the CNTs bundles by the strong HF acid treatment.

The as-grown CNR morphology was observed by the field emission scanning electron microscopy (FESEM), with EDS. The structural and side wall defects of CNR was examined by high resolution transmission electron microscopy (HRTEM). The structural quality and orientation of rings were analyzed by Laser Confocal Raman Spectrometer with Microscope. X-ray diffraction (XRD) analysis was carried out using Mini Flex 300/600 –

Benchtop X-ray diffractometer. The surface functionalization of rings was studied by Fourier transform infrared spectroscopy (FTIR).

3.0 RESULTS

The morphology of NiO/Al_2O_3 catalyst particles is shown in Fig.1a. The particles are spherical in shape and agglomerated. Fig.1b shows EDAX analysis image of NiO/Al_2O_3 catalyst particles. Fig.2 shows the FESEM images of CNR at different magnifications and in different spots of the sample. Since no purification treatment was performed on the sample before the FESEM characterization, the CNR structure obtained are as synthesized. Fig.2a clearly reveals that the high yield of CNRs as indicated by an arrow mark and some of the straight nanotubes are also observed in the sample. Fig.2b shows the grown rings having a well-defined ring structure, along with rings. The CNTs, amorphous carbon and catalyst particles are also present in the sample because of the as-grown samples are not purified during of FESEM analysis. Fig. 2c is the higher magnification image of the fig.2b. It is clearly evident from this figure that straight nanotubes were connected to form the rings. The presence of a catalyst particle at the tip of the rings are indicated by an arrow mark. Hence, it is concluded that CNR was synthesized by tip growth mode depicted in fig.2d.

There is no open literature available revealing the growth mode of CNR, especially in MWCNRs. The rings typically have thickness ranges from 7 to 17 nm and diameter ranges from 10 to 190 nm. **Ahlskog.et al.** [11], reported that CNR synthesized by CVD process has a thickness of 11 to 21 nm and a diameter of 400 nm, which is larger than the results obtained in this investigation. Fig.2e shows the bundles of CNTs synthesized at the flow rate of 140 ml/min precursor gas. The image 2e clearly shows the straight nanotubes and shows the presence of some of the curved nanotubes.

The HRTEM image of CNR is shown in Fig.3. Most of the rings were fractured rings as shown in fig.3a, due to strong HF acid treatment procedure that was employed in the extraction step. Fig.3b depicts the individual CNR with well-oriented structure. Fig.3c represents the Ring, where the inner and outer diameter of the rings clearly visible and it could be confirmed as the MWCNR. The image 3c also reveals the MWCNR with sidewall defects and the rings are buried under the amorphous carbon.

Raman spectroscopy analysis was employed on the MWCNRs mainly to study the structure and orientation of the rings. When CNTs is subjected to Raman spectroscopy analysis, usually it consists of two main peaks; G and D band. But G band of ring shows new features compared to straight nanotubes, as shown in fig.4. The Raman spectra of G band were split into two components, i.e., G^- and G^+. The results of Raman spectra of the rings are

matching with the work done by **Ren. et. al,** [17]. In order to analyze the G band peaks, the spectra was normalized to obtain the area, full width half maximum (FWHM) and peak intensity using Gaussian peak functions. The analysis was a failure due to the lower intensity of the G^- band. However, G^+ band peak, which has a higher intensity, was analyzed and the obtained result is presented in table 1. **Wang et. al,** [18], synthesized SWCNRs using Pickering emulsion-based processes and the FWHM value was similar to this investigation. They obtained FWHM value in between 50 to 60 cm^{-1}, for CNR diameter of 150 to 300 nm. Fig.4 also shows the Raman spectra peaks of the linear MWCNTs, which indicates the absence of G^- band spectra.

XRD analysis of rings is shown in fig.5, which clearly reveal the amorphous nature of the sample after the HF acid treatment of the extraction process. The only observed peak was 21.73 theta. The MWCNTs peak of 25.8 (002) (JCPDS card no. 26-1079) as proposed by **Liu et. al,** [19], which is close to the rings XRD pattern of 21.73 theta. The diffraction angle (d), FWHM of XRD peaks of CNRs were calculated and presented in table 2.

The FTIR spectra of MWCNRs in the range between 500 to 4000 cm^{-1} is shown in fig.6. The 1658 cm^{-1} peak is attributed to the graphitic mode and in between 830 to 930 cm^{-1} two sharp peaks are observed, which resembles the graphitic mode peak of 1658 cm^{-1}. The peak at 1503 cm^{-1} is assigned to the D band. Taking consideration of the peak wavenumbers of **Branca et. al,** [20], depicted FTIR results in oxidative nature of MWCNTs, compared to that FTIR peak, the peak of the rings is shifted up to higher wavenumbers.

4.0 DISCUSSION

The MWCNR structure, analytical characterization, and functionalization are presented and discussed briefly in the results section. The first step of this investigation was to synthesize agglomerated catalyst. **Song et. al,** [13], proposed that CNTs in bundles grow with different growth rates due to the different extrusion velocities of carbon atoms on the catalyst particles. It is believed that CNT bundles will curve due to the stress induced between the two nanotube walls inside the bundles. To enhance the bending moment of the CNT walls, the agglomerated catalyst was synthesized, which will facilitate the growth of two nanotube walls as far as nearer to each other. This reduction in space between the two nanotube walls promotes the curvy nature of CNTs. In this investigation it is found that the MWCNRs has grown as tip growth mode. The growth of CNTs is mostly tip growth mode in the catalytic CVD process.

The catalyst particles are in active mode at elevated temperature, at the flow of precursor gas, the growth rate of nanotube varies with respect to flow rate of precursor gas due to the different extrusion velocity of carbon atoms on the catalyst particles. This leads to the nanotube walls curve with each other, due to induced thermal stress.

The catalyst particles are freely supported on the alumina boat, that facilitates to carry the particles at the tip of the nanotube.

The bending nature of the tube may be facilitated through these three mechanisms,

(i) The stress induced between the two walls of nanotube that bend the tube into the toroidal structure.

(ii) The tip of the nanotubes should be weighed compared to the bottom due to the presence of catalyst particles and it led to the slope or bend the nanotubes, towards the flow direction of precursor gas.

(iii) Both the stress-induced curvature and bending due to the velocity of precursor gas along with a weighed tip of the tube occurs in a parallel way to enhance the curvature nature of the straight tubes.

The open ring of MWCNTs is shown in fig.3a. The formation mechanism for open ring MWCNTs is depicted in fig.7. Fig.7a shows the active catalyst particle in an elevated temperature, the extrusion velocity of carbon atoms on catalyst varies with each particle in the substrate. This results in mismatch growth in nanotubes regarding the length of the nanotube walls as depicted in fig.7c. The bending nanotube eating its own tail is depicted in fig.7d. Though the nanotube tail is attached with the catalyst particles, which claim to be tip growth mode of MWCNTs. While conducting the extraction treatment on the ring samples using HF acid, the catalyst particles are dissolved and result in open ring MWCNTs as shown in fig.7e.

Song et. al, [21], studied the Raman spectroscopy on the SWNTs rings, where the spectra split into several peaks. The Raman spectra obtain in this investigation is also split into more peaks (fig.4). The FTIR image (fig.6) shows a functional group attached with rings and peaks are shifted to higher wavenumbers due to the decrease in bond length. Since the curvature reduces the bond length of the tube which results in a higher shift in peak wavenumbers. Fig.2e shows the FESEM image of nanotubes synthesized at a flow rate of precursor gas 140 ml/min and it has abundant of the straight nanotube and there is no evidence of curved nanotubes. This effect clearly clarifies that extrusion of carbon atoms on catalyst particle variation is not influenced as much as compared to 180 ml/min precursor gas flow rate, which results in straight nanotubes. Hence, as anticipated by **Song.et.al,** [13], the flow rate of precursor gas has a significant effect on the curvature of CNTs.

Though **Ko et. al,** [22], synthesized open ring nanotubes by ultrasonication process, CCVD process employed in this investigation is also a viable route to synthesize open ring MWCNTs and it will pave way for large-scale production.

5.0 CONCLUSIONS

(i) A new combination of agglomerated catalyst particles (NiO/Al_2O_3) have been synthesized to produce Multi-Walled Carbon Nano Rings.

(ii) A new procedure has been developed to synthesize MWCNRs by thermally decomposing acetylene in a catalytic CVD process.

(iii) It is found that the flow rate of precursor gas has greater influence on the bending nature of nanotubes.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest

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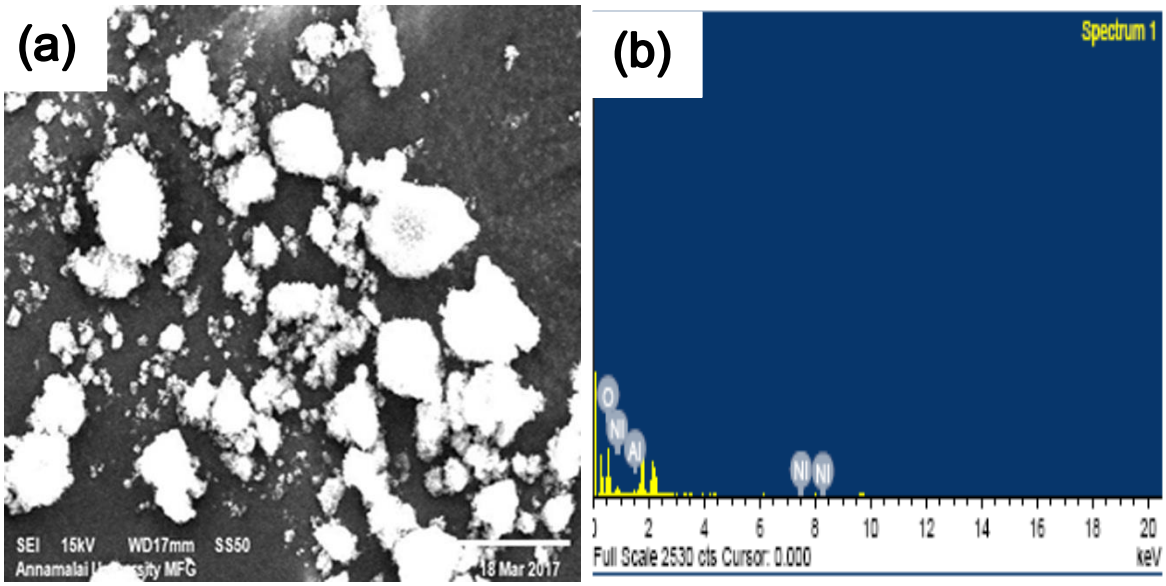

Fig.1 (a) FESEM image of agglomerated NiO/Al_2O_3 metal catalyst (b) EDAX analysis image shows the presence of Ni, Al, and O elements

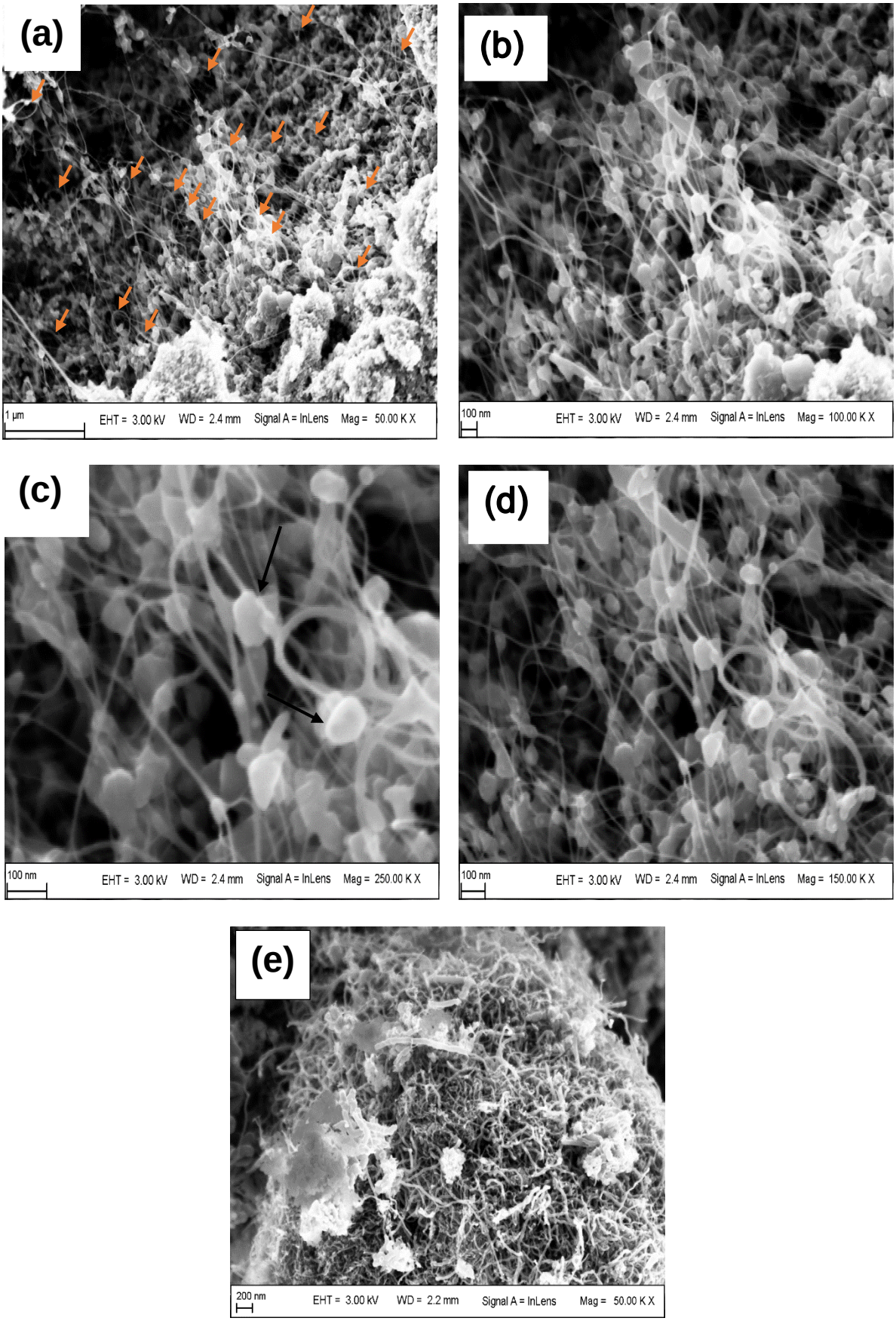

Fig.2 FESEM image (a-d) CNRs image at different magnifications at various spots of the sample (e) Image of straight nanotubes synthesized at different CVD process condition

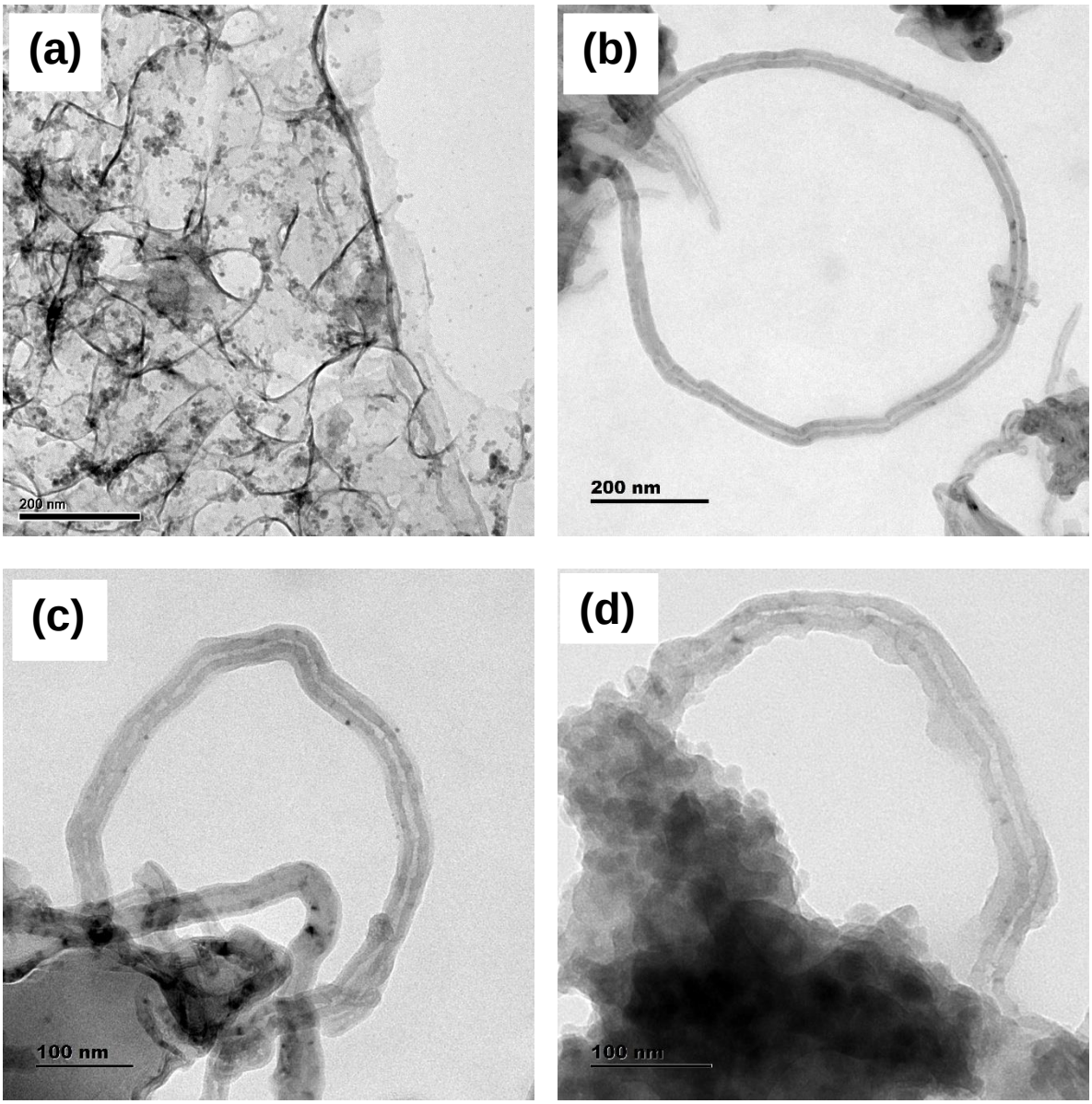

Fig.3 HRTEM images of open ring MWCNTs

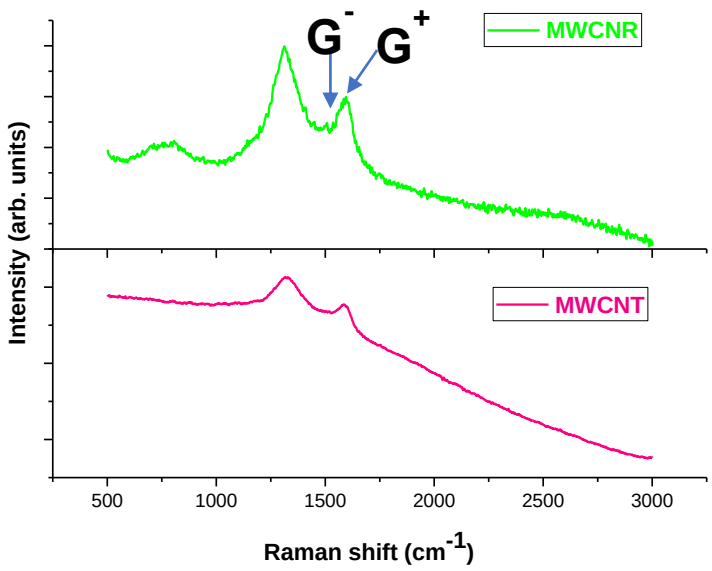

Fig.4 Raman spectra of carbon nano rings (Green peaks) and straight nanotubes (purple peaks)

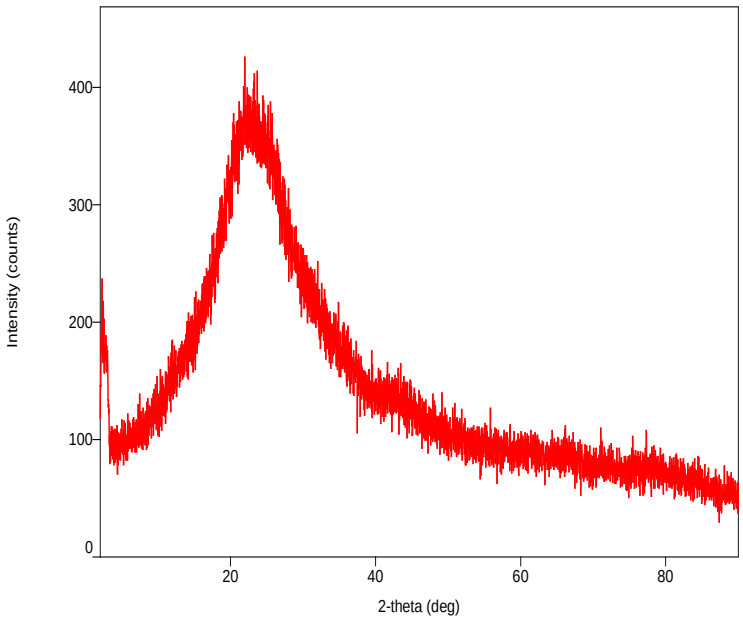

Fig.5 XRD peak of carbon nano rings

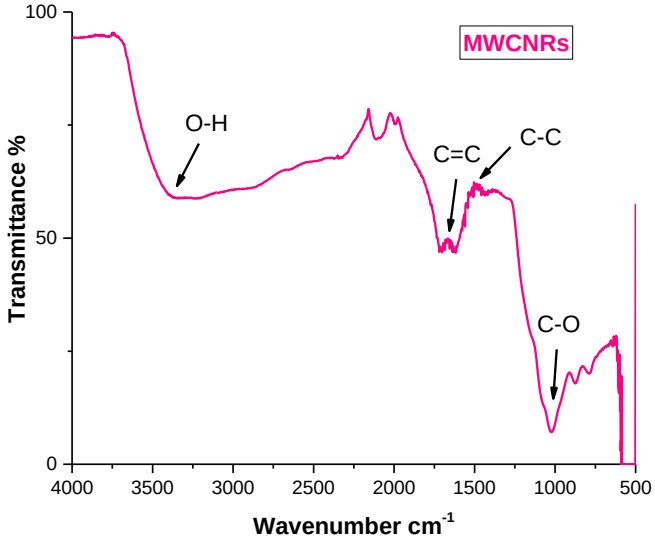

Fig.6 FTIR peaks of carbon nano rings

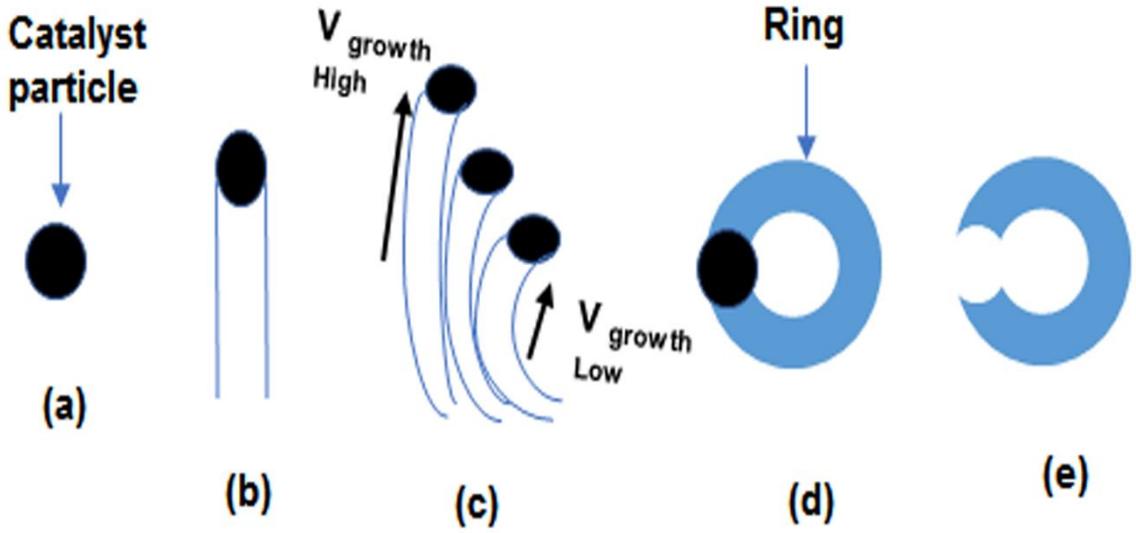

Fig.7 (a-d) Growth mechanism of carbon nano rings (e) open ring structure

No	Band	Intensity	FWHM	I_D/I_G RATIO
1.	G^+	1594 cm^{-1}	54 cm^{-1}	1.56

Table 1 Raman spectra analysis of CNRs peaks

No	2-theta (deg)	D (ang.)	Height (counts)	FWHM (deg)
1.	21.73	4.09	153	13.89

Table 2 XRD peak results of CNRs