

Carbon nanotubes, nanorings, and nanospheres: Synthesis and fabrication via chemical vapor deposition—a review

Nanomaterials and Nanotechnology
Volume 12: 1–21
© The Author(s) 2022
Article reuse guidelines:
sagepub.com/journals-permissions
DOI: 10.1177/18479804221079495
journals.sagepub.com/home/nax


V Sivamaran¹ , V Balasubramanian², M Gopalakrishnan³, V Viswabaskaran⁴,
A Gourav Rao⁵ and ST Selvamani⁶

Abstract

Research work published since 2010 on the synthesis of carbon nanotubes (CNTs), carbon nanorings (CNRs), and carbon nanospheres (CNSs) using the chemical vapor deposition (CVD) process is reviewed. The effect of CVD process parameters on carbon nanomaterials morphology, such as diameter, yield, and quality was reviewed. The mechanism of CVD formation and growth of carbon nanomaterials was reviewed in detail. The catalyst materials used to synthesize these carbon allotropies were discussed in detail. The formation mechanism of carbon nanomaterials indicates that the variables of the CVD process parameters that appear to control growth are not directly manipulated in the CVD process. Rather, it is determined by complex interactions between variables. The impact of CNTs, CNRs, and CNSs was discussed using the schematic representation. The researchers who published the articles in the CNTs, CNRs, and CNSs for the past decade were discussed. From the intensive literature review, it was found that as compared to CNTs there is not much research was undertaken in synthesizing spheres and rings. But spheres and rings are capable of performing better than CNTs structure in energy storage, and sensors.

Keywords

Carbon nanotubes, carbon nanorings, carbon nanospheres, chemical vapor deposition process

Date received: 28 August 2021; accepted: 24 January 2022

Topic Area: Low Dimensional Semiconductor and Graphene-like Nanostructures

Topic Editor: Leander Tapfer

Associate Editor: Paola De Padova

Introduction

Carbon can form different allotropic structures composed entirely of carbon but with different physical and chemical structures, such as graphite, graphene, diamond, fullerene, carbon black (CB), graphite nanofiber (GNF), carbon nanotubes (CNTs), nanorings carbon (CNRs), and carbon nanospheres (CNSs).^{1,2} Among these carbon allotropies, CNTs were found to be key nanomaterial because of their superior unique properties. Since Iijima, (1991)³ found CNTs accidentally while synthesizing fullerene by arc discharge method, undoubtedly it became the headlines of nanotechnology due to their unique mechanical,^{4,5} thermal, and electrical properties.^{6,7} Recently,

¹Department of Mechanical Engineering, Audisanakara College of Engineering and Technology, Gudur, Andhra Pradesh

²Department of Manufacturing Engineering, Annamalai University, Annamalai Nagar, Tamil Nadu

³Department of Chemistry, Annamalai University, Annamalai Nagar, Tamil Nadu

⁴VB Ceramic Research Centre, Chennai, Tamil Nadu

⁵DRDO Naval Materials Research Laboratory, Mumbai, Maharashtra

⁶Chennai Institute of Technology, Chennai, Tamil Nadu

Corresponding author:

Sivamaran V, Department of Mechanical Engineering, Audisanakara College of Engineering and Technology, Gudur 524101, Andhra Pradesh. Email: sivamaranv@gmail.com



Creative Commons CC BY: This article is distributed under the terms of the Creative Commons Attribution 4.0 License (<https://creativecommons.org/licenses/by/4.0/>) which permits any use, reproduction and distribution of the work without further permission provided the original work is attributed as specified on the SAGE and Open Access pages (<https://us.sagepub.com/en-us/nam/open-access-at-sage>).

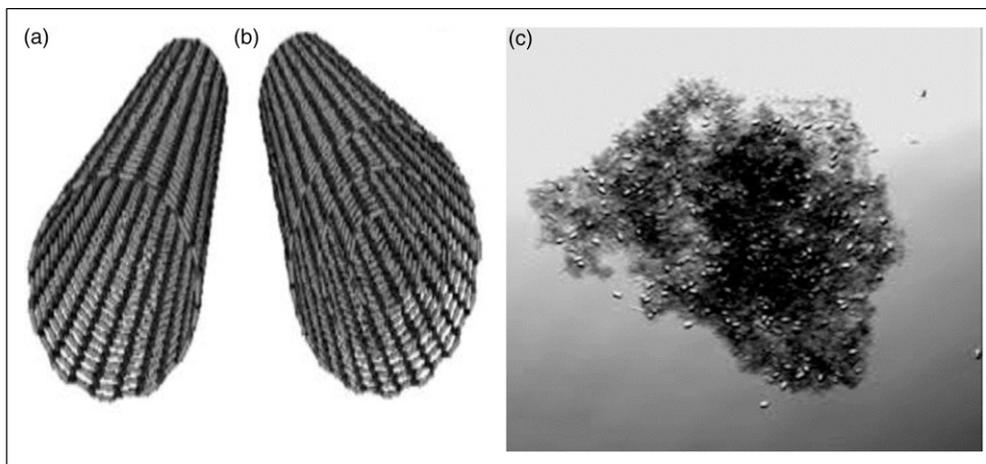


Figure 1. Schematic structure of CNTs (a) SWCNTs; (b) MWCNTs; (c) visible of CNTs in naked eyes (Eatemadi et al. (2014)¹⁷).

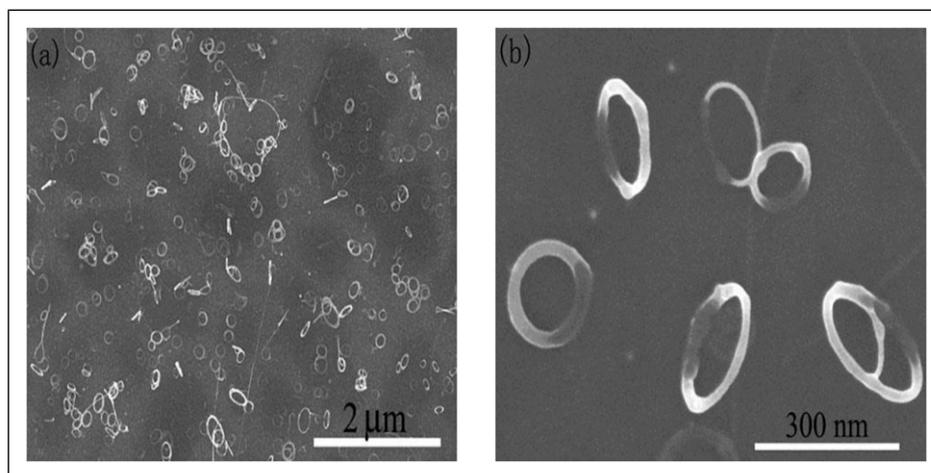


Figure 2. a) Low; b) high-magnification SEM images of SWNT rings deposited on a silicon substrate Song et al. (2006).¹⁹

toroidal CNTs catch the attention of researchers because they can be used directly as a nanoscale device.⁸ In the last 10 years, due to the enormous potential of CNS in the storage and conversion of energy, the synthesis of carbon spheres has attracted researchers.^{9–15} Even some researchers have tried to combine the synthesis of CNTs, and/or CNSs, CNRs,¹⁶ which may be possible by optimizing the process parameters. Moreover, the multi-layered fullerenes, also known as onion-like carbons or carbon nano-onions seem to promising in the biomedical applications.^{17,18} Therefore, the purpose of this review is to update the knowledge on the use of chemical vapor deposition processes to synthesize carbon nanomaterials (such as CNT, CNR, and CNS).

For the naked eye, CNTs will look like black charcoal powder (see Figure 1(c)), but at higher magnification, they will be visible as cylindrical structures. If a single graphene sheet is rolled, it is called SWCNT (Figure 1(a)) and multiple graphene sheets are rolled it is called MWCNT (Figure 1(b)). If the CNTs are rolled as a ring, then it is called CNRs (Figure 2). If

the carbon forms like a football shape then it is called Carbon CNSs (Figure 3).

There are many methods for synthesizing carbon nanotubes, including arc discharge, laser ablation, and chemical vapor deposition (CVD) processes. For a long time, arc discharge and laser ablation have been the primary methods for obtaining near-perfect single-walled carbon nanotubes and multi-walled carbon nanotubes. There are several questions about these methods. First, both methods rely on the evaporation of carbon atoms from a solid carbon source at 3000° C, which is not efficient and limits the amplification of CNTs. Second, the nanotubes synthesized by the evaporation method are in the form of entanglements, which are difficult to purify, manipulate, and assemble to build addressable nanotube structures.^{21,22} The schematic diagram of the CVD process is shown in Figure 4.

Compared to laser ablation and arc discharge methods, CVD is a simple and inexpensive technique for synthesizing CNTs at low ambient temperature and pressure. In terms of crystals, arc and laser grown carbon nanotubes are better than CVD grown

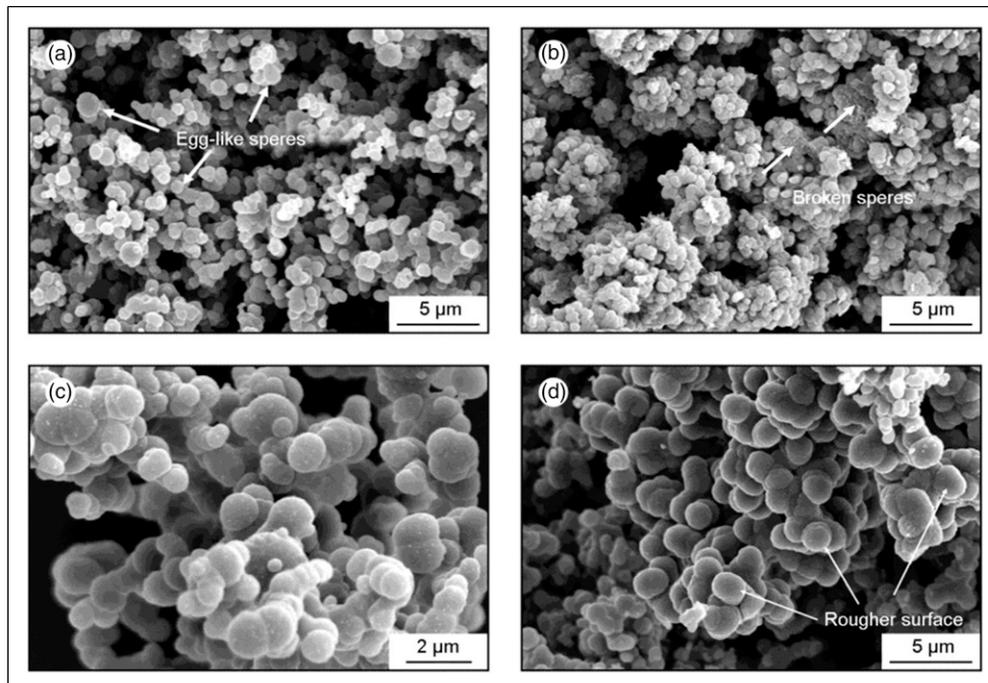


Figure 3. SEM images of carbon spheres, synthesized using the natural gas/H₂ at flow ratio of 1:1 and at different deposition temperatures (a) 1070°C, (b) 1100°C, (c) 1150°C, and (d) 1200°C (Zhang et. al., (2016))²⁰

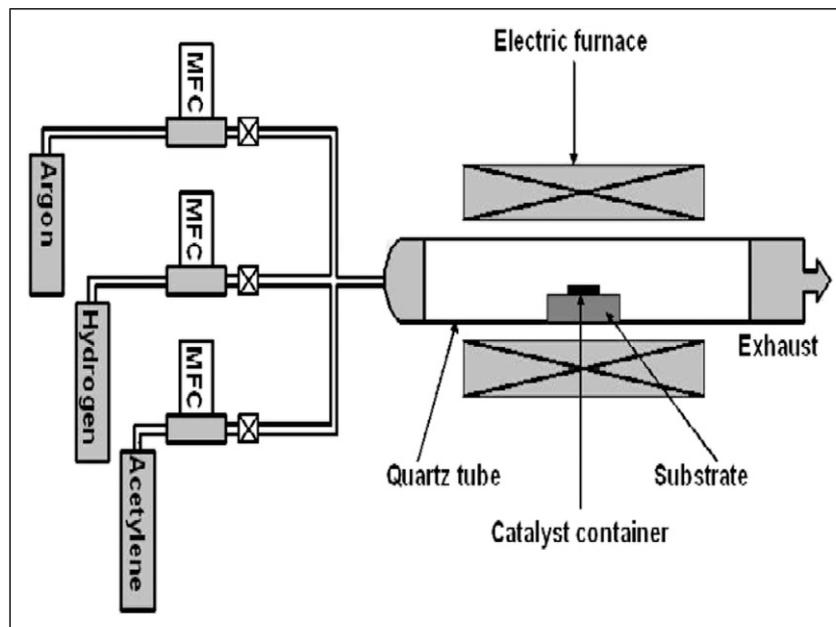


Figure 4. Schematic diagram of the CVD set-up (Nourbakhsh et al. (2007)).²³

carbon nanotubes. However, CVD outperforms arc and laser methods in terms of performance and purity. Also, CVD is the only answer when building the controller CNT architecture. CVD is versatile because it can use a large amount of hydrocarbons in any state (solid, liquid or gas), it can use a variety of substrates and it allows the growth of CNT in various forms, such as powder, thin or thick film, lined or

entangled nanotubes, straight or coiled, or desired nanotube structures at predetermined locations on a patterned substrate. It can also better control growth parameters.²⁴ Table 1 shows a summary and comparison of the three most common CNT synthesis methods.

The main aim of this investigation is to review the literature (See Table 2) on CNTs, CNRs, and CNS

Table I. Summary and comparison of three most common CNT synthesis methods (Eatemadi et al., (2014)).¹⁷

Method	Arc discharge	Laser ablation	CVD
Yield rate	>75%	>75%	>75%
SWNT or MWNT	Both	Both	Both
Advantage	Simple, inexpensive, high-quality nanotubes	Relatively high purity, room temperature synthesis	Simple, low temperature, high purity, large-scale production, aligned growth possible
Disadvantage	High temperature, purification required, tangled nanotubes	Method limited to the lab scale, crude product purification required	Synthesized CNTs are usually MWNTs, defects

synthesis via the CVD process. Table 2 shows a list of articles that were published in the synthesis of different allotropies of carbon up to the year 2020. The criteria for this review paper include the type of CVD chamber, catalyst material used, type of carbon structure obtained, the effect of CVD process parameters like reaction temperature, the flow rate of a precursor gas, and reaction time were summarized.

Carbon nanotubes

The growth mechanism of carbon nanotubes has been controversial since their discovery. Based on CVD response conditions and purification analysis, some researchers have proposed more than a few often conflicting possibilities. Thus, until now, not even one CNT growth mechanism has been well established. On the other hand, the most common and widely accepted mechanism can be summarized as follows. When steam from the precursor gas comes into contact with the “hot” metal catalyst particles, it first breaks down the carbon atoms and hydrogen atoms, the hydrogen atoms fly away, and the carbon atoms dissolve into the catalyst metal. After reaching the solubility limit of the carbon atoms in the catalyst metal at this reaction temperature, the dissolved carbon begins to accumulate in the vertical direction. The decomposition of precursor gases (hydrocarbons) (as an exothermic process) releases some heat to the catalyst metal, while the crystallization of carbon (as an endothermic process) absorbs some heat from the catalyst metal precipitation zone²⁴.

As shown in Figure 5, there are two general cases, in case one (Figure 5(a))

1. When the catalyst-substrate interaction is weak, the precursor gas (hydrocarbon) decomposes on the upper surface of the catalyst metal, carbon diffuses downward through the catalyst metal, and CNTs precipitate through the bottom of the metal, expelling all metal particles. Substrate.
2. As long as the top of the metal is open to the decomposition of fresh precursor gas, the CNT will continue to grow larger.

3. Once the catalyst metal is completely covered by excess carbon atoms, its catalytic activity will stop and the growth of the carbon nanotubes will also stop, which is called the “tip growth model.”⁴³

In the second case, (Figure 5(b)) when the catalyst to substrate interaction is strong, initial hydrocarbon decomposition and carbon atoms diffusion take place similar to that in the tip-growth case, but the CNT precipitation fails to push the metal particle up; so the precipitation is forced to emerge out from the top of the catalyst metal.

1. First, the carbon crystallizes into a hemispherical dome, and then extends upward into a seamless graphite cylinder.
2. Subsequent deposition of hydrocarbons occurs on the lower peripheral surface of the catalyst metal and diffuses upward with the dissolved carbon atoms. Therefore, the catalyst particles take root at the bottom when CNTs grow; therefore, this is called the “base growth model.”⁴⁴

Effect of CVD process parameters on CNTs growth

CNTs synthesized using the CVD process have various process parameters that control the final structure of CNTs.³⁰ Hence, in these section main CVD process parameters such as reaction temperature, the flow rate of a precursor gas, and reaction time and their effect on CNTs structure will be discussed.

Effect of temperature on CNTs growth. Researchers grown CNTs on Ni catalyst films using methane at 900°C show poor coverage (see Figure 6) which may be due to the lack of nickel islands formed on the copper surface to catalyze the growth of CNT. The diameter of CNTs grown with a methane source is larger than that of carbon nanotubes grown with an acetylene source at a lower temperature. CNTs grown in acetylene at 650°C show better coverage and are smaller in diameter. Raman data also shows that the quality of CNTs grown is better using the acetylene source at 650°C. The authors concluded that acetylene is a better

Table 2. Summary of important articles in carbon nanomaterials synthesis via CVD process from 2010 to present

Ref. No and author details	Type of CVD chamber/process	Catalyst material used	Catalyst form (bulk/powder)	Reaction Temp. (°C)	Precursor gas	Flow rate of precursor gas	Reaction time (mins)	Outcome
Sivakumar. et al. 2011 ²⁵	Thermal CVD	Fe and Ni	Powder	750°C	N ₂ /CH ₄ and H ₂ /CH ₄	120:120 ml/min and 1:2 (120:240 ml/min)	—	MWCNTs
Awadallah. et al. 2012 ²⁶	Thermal CVD	Ni–Mo and Co–Mo supported on Al ₂ O ₃	Powder	700°C	Natural gas	25 ml/min	60	MWCNTs
Tyagi. et al. 2011 ²⁷	Thermal CVD	Cu and Au	Grid used for TEM specimens	900°C	CH ₄	100 ml/min	30	MWCNTs
Kruszka. et al. 2014 ²⁸	Horizontal and vertical	Copper	Metal surface	1073°C–1273°C	CH ₄	—	15–40	CNTs
Pinilla. et al. 2010 ²⁹	Fluidized bed reactor (FBR)	NiCu/Al ₂ O ₃	Powder	700°C	CH ₄	—	420	CNTs
Ch Das. et al. 2011 ³⁰	Thermal CVD	Si (100) - Al and Fe	Metal surface	—	Ferrocene	4 mg/h of thermally evaporated ferrocene	—	CNTs
Atthipalli. et al. 2011 ³¹	Thermal CVD	Copper foil using a Nickel thin film	Metal surface	900°C	CH ₄ and acetylene	690 sccm	30	CNTs
Tripathi. et al. 2014 ³²	Thermal CVD	Silicon wafer where a predeposition of iron catalyst of 2 nm thickness was made by sputtering	Metal surface	1000°C	acetylene	10 to 50 sccm	6–14 min	CNTs
Fathy. et al. 2017 ³³	Thermal CVD	Rice straw, Fe–Ni	Powder	800°C	Camphor	—	120 min	MWCNTs
Ahmad. Et. al. 2019 ³⁴	Floating catalyst chemical vapor deposition	Monometallic (Fe, Co, Ni), bimetallic (Co–Ni, Co–Fe)	Rod and tube electrodes	1050°C	Ethylene	500 sccm	10 s	SWCNTs
Sun et al. 2012 ³⁵	Thermal CVD	CoAl–DSO–MMA–LDH	Metal surface	800°C	Two-dimensional interlayer galleries of a layered double hydroxide (LDH)	—	20 ml/min	CNRs
Wang. et al. 2012 ³⁶	Pickering emulsion-based method	SWCNTs	Powder	—	SWCNT (0.65 mg), DCB (6.5 g), and a few drops of ethanol were added to a test tube.	—	—	SWCNRs
Lei. et al. 2011 ³⁷	Catalytic CVD	La, Nb, and Ti, dispersed on porous kaolin support	Powder	720–810°C	C ₂ H ₂	70 sccm	10 min	CNSs

(continued)

Table 2. (continued)

Ref. No and author details	Type of CVD chamber/process	Catalyst material used	Catalyst form (bulk/powder)	Reaction Temp. (°C)	Precursor gas	Flow rate of precursor gas	Reaction time (mins)	Outcome
li. et al. 2016 ³⁸	Metal catalyst-free chemical vapor deposition (CVD)	SiO ₂ spheres or Au@SiO ₂	Powder	1100–1200°C	Methane	5 sccm	1–10 min	Hollow carbon spheres
Zhang. et al. 2016 ³⁹	Catalytic chemical vapor deposition	—	—	1150°C	CH ₄ and H ₂	500 sccm	2 h	Carbon spheres
Reyna. et al. 2020 ⁴⁰	one-step chemical vapor deposition (CVD) process	Iron-nickel nanoalloy	Powder	—	—	—	3 h	Carbon nanospheres with an encapsulated iron-nickel
Qu. Et. al. 2010 ⁴¹	Plasma-enhanced chemical vapor deposition (PECVD)	Fe was vacuum deposited on an SiO ₂ /Si	Metal surface	750°C	C ₂ H ₂	50–80 mTorr	10 min	Carbon nanospheres
D D Saputri ⁴²	CVD				Biogas-based carbon precursor			

choice for large-scale synthesis of MWCNTs in copper using Ni catalytic film than methane.³¹

Authors also reported the growth of carbon nanomaterials including CNTs and carbon onions were manufactured on nano-sized Ni/Al catalysts at 450–600° C using the CVD methane process (see Figure 7). The author used transmission electron microscopy and X-ray energy dispersive spectroscopy to characterize carbon nanomaterials, and studied the influence of Ni/Al catalyst composition and reaction temperature on the morphology of carbon nanomaterials. The results showed that carbon nanotubes and carbon onions were synthesized at moderate temperatures. The composition of the Ni/Al catalyst and the reaction temperature has a great influence on the morphology of carbon nanomaterials. When a relatively high reaction temperature (550–600°C) and a relatively low nickel content (60% by weight) catalyst are used, pure carbon onions can be obtained.⁴⁵

Effect of precursor gas flow rate on CNTs growth. Shukrullah et al. (2015)⁴⁶ conducted a systematic study on the optimization of the CVD process parameters to study the diameter distribution of the MWCNTs grown on Fe₂O₃/Al₂O₃ catalyst support at a fixed temperature of 800°C. FESEM and TEM techniques were used to quantify the influence of the flow rate of ethylene and the CVD process time in the CNT growth parameters. At a critical ethylene flow rate of 100 sccm and a CVD treatment time of 60 min, these studies observed dense and uniform growth of relatively pure nanotubes with a longer tube length and a narrow diameter distribution (see Figure 8).

Under optimal conditions, the growth of carbon nanotubes has the narrowest diameter distribution, which is 20–25 nm. Furthermore, under these operating conditions, the low surface defects and impurities, the high yield percentage and the graphite structure of the growth tube are obvious. In the optimized parameters of the CVD process, there is a balance between the decomposition rate of C₂H₄ and the diffusion rate of carbon in the Fe₂O₃/Al₂O₃ catalyst particles. The C₂H₄ flow rate is less than 100 sccm and there are not enough reactants (carbon atoms) to react with the metal particles to make the most of the available catalyst. Due to the lower availability of catalyst particles, when the flow rate is greater than the optimal value, the concentration of the carbon source will not significantly affect the decomposition or the growth rate of CNT.

Effect of process time on CNTs growth. According to Zhan et al., in 2007,⁴⁷ a high flow rate can prolong the residence time of the hydrocarbon gas on the catalyst surface, thus producing a good carbon nanotube structure (see Figure 9). Furthermore, high precursor gas flow rates tend to increase the decomposition rate of hydrocarbons, resulting in higher yields of carbon products. Tripatti et al. 2014³² studied the influence of acetylene flux and treatment time on CNT growth. It is observed that the performance and the length of the pipeline decrease linearly with the flow rate and the time of the precursor gas. Contradicting the

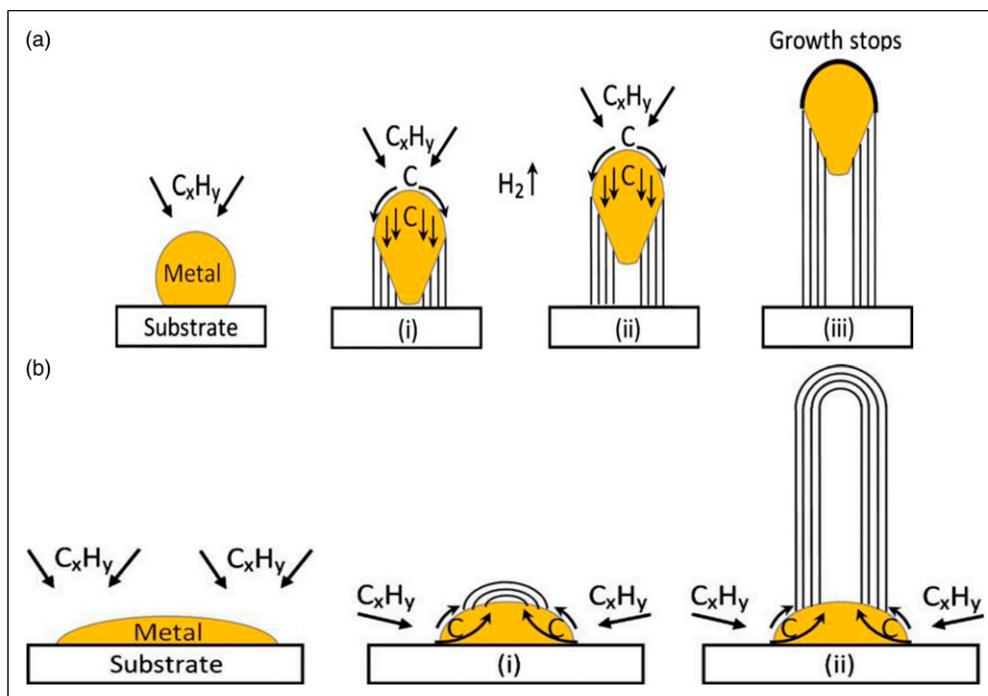


Figure 5. The growth mechanisms for CNTs: (a) tip-growth model, (b) base growth model⁴⁴.

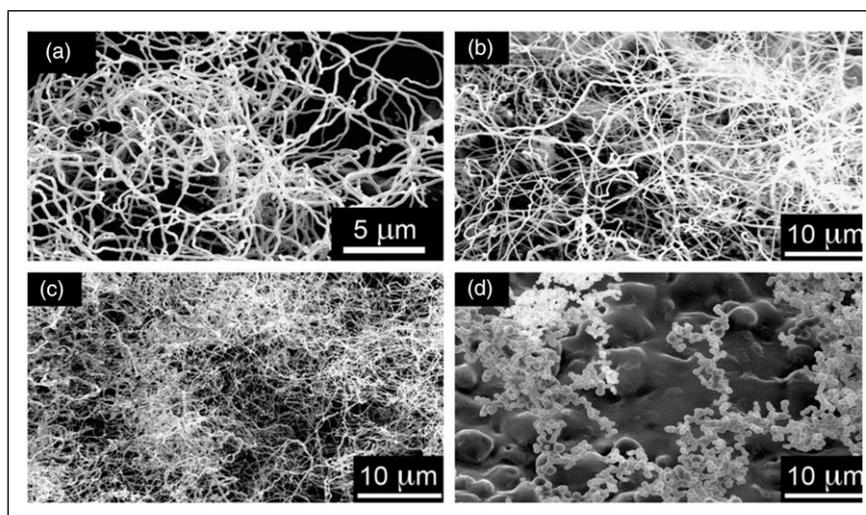


Figure 6. SEM images of the CNTs grown using different nickel film thicknesses using methane as the carbon source: (a) 20 nm, (b) 30 nm, (c) 45 nm, and (d) 60 nm. Atthipalli et al 2011³¹.

above statement some authors reported that the morphology of carbon nanotubes does not depend on carbon feedstocks, especially when specific catalysts are used in the process.^{48,49}

Influence of catalyst particles on CNTs growth

In order to synthesize CNTs using the CVD process, nano-sized metal catalyst particles are generally required to allow the decomposition of hydrocarbons at a temperature lower

than the spontaneous decomposition temperature of hydrocarbons.

The most commonly used metals are Fe, Co, Ni because for two main reasons (see Table 3):

1. The high solubility of carbon in these metals at high temperatures; and
2. The high diffusivity of carbon atoms in these metals. In addition, the high melting point and low equilibrium

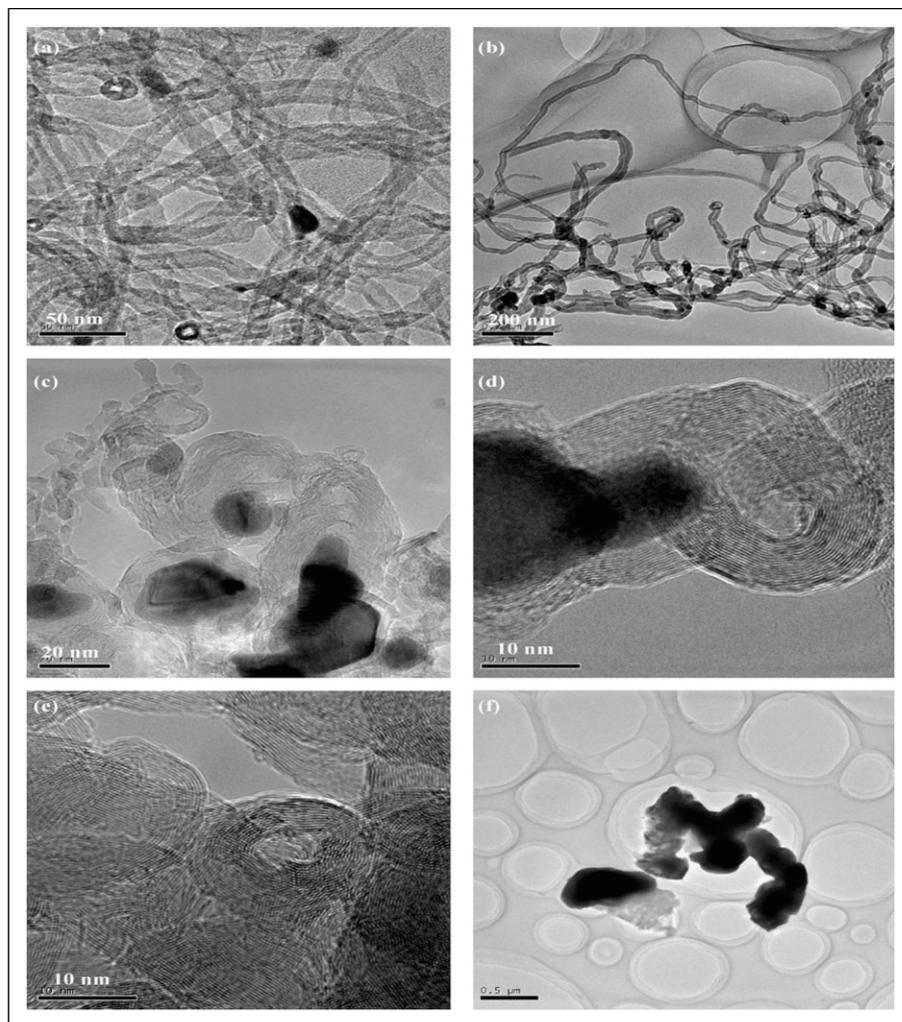


Figure 7. TEM images (a) CNTs obtained using Ni/Al catalyst with 5 wt% of Ni, (b) CNTs obtained using Ni/Al catalyst with 20 wt % Ni, (c) mixture of CNTs and carbon onions obtained using Ni/Al catalyst with 40 wt % of Ni, (d) carbon onions obtained using Ni/Al catalyst with 60 wt % of Ni, (e) carbon onions obtained using Ni/Al catalyst with 80 wt % of Ni, and (f) the products (without any carbon nanomaterials) obtained using 100 wt % Ni (He et al (2009)).⁴⁵

vapor pressure of these metals provide a wide CVD temperature window for various carbon precursors.

Researchers have conducted more experiments and used different types of transition metals as catalysts to find the suitable catalyst system to synthesize CNTs via CCVD process. Shin. et. al., (2006)⁵⁰ reported that methane was used as a carbon source to synthesize CNTs and obtain MWCNTs in an Al-supported Ni catalyst. Sivakumar. et. al., (2011)²⁵ reported that used catalytic CVD process to synthesize multi-walled carbon nanotubes, using methane as the precursor gas and nickel as the metal catalyst. In this report, it was found that the Ni catalyst showed a methane conversion rate of 42%. Mendoza et al. 2005⁵¹ synthesized MWCNT using a catalytic CVD process, and reported the influence of Co. Awadallah et al. 2012²⁶

synthesized CNTs by a CVD process using Ni-Mo-Al and Co-Mo-Al. In this report, the author has concluded that the Ni-Mo-Al catalyst gave higher purity of CNTs compared to the Co-Mo-Al catalyst. Tyagi et al., (2011)²⁷ CNTs synthesized using Cu grid, commonly used as TEM specimen support. In this report, the author concluded that the Cu does not seem to be suitable for CNTs growth. Kwszka et al., (2014)²⁸ reported that three different types of CVD, such as vertical, horizontal, and quartz tubes, were used to grow CNT using Cu thin films. In this report, the addition of additional sulfuric acid to the Cu catalyst film was found to promote CNT growth.

The researchers also used bimetallic catalysts to synthesize carbon nanotubes through a CVD catalytic process. Li et al. 1997⁵² used Ni/Cu/Al catalysts to synthesize CNTs through a catalytic CVD process, and reported that the

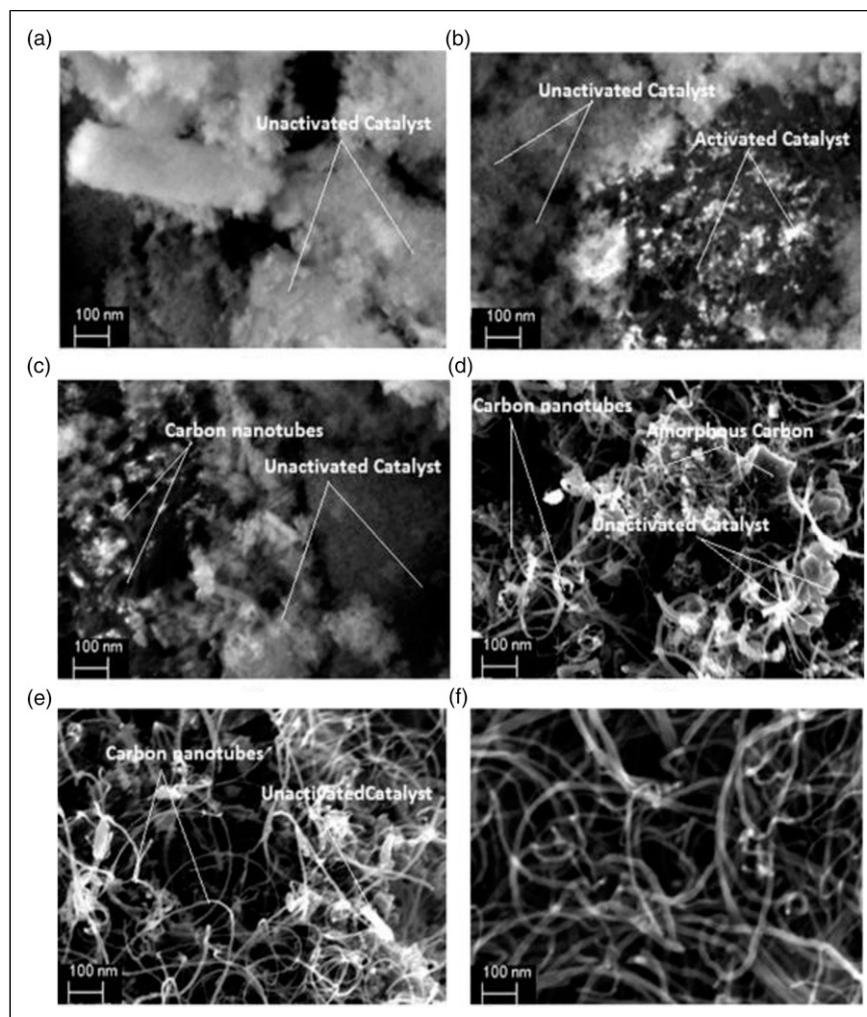


Figure 8. TEM of CNTs grown using ethylene at flow rates of; (a) 60 sccm, (b) 80 sccm, (c) 100 sccm and (d) 110 sccm (Shukrullah et. al., (2015)).⁴⁶

addition of Cu to Ni particles improves the catalytic growth efficiency of CNTs. Pinilla et al., (2010)²⁵ studied the different operating conditions of a fluidized bed CVD reactor, which played an important role in the performance of the carbon deposition of the NiCu/Al₂O₃ catalyst (see Figure 10) for the decomposition of methane. Shlyachova et al., (2009)⁵³ CNTs were synthesized by the CCVD process using Ni, Co, and Ni/Co catalysts supported by calcium tartrate. In this research, the authors concluded that they found that CNTs grown on these catalysts have similar morphologies, but have different degrees of graphitization. NC Das et al., (2011)³⁰ Using two layers of metal catalyst of 10 nm Al and 1 nm Fe, vertically aligned MWCNTs (CNTs) were synthesized on Si (100) wafers by a CVD process. In the author of this report, through the adjustment of the SAXS spectrum model, the true change in the CNT diameter of the vertically arranged MWCNT was quantitatively characterized. The mean diameter of CNT is

found to increase with increasing distance from the substrate. Sivamaran. et. al. 2019⁵⁴ use six different monometallic and bimetallic catalysts (NiO, CoO, CuO, NiO/CuO, NiO/CoO, CoO/CoO) in a single experiment (run) using a single-step catalytic chemical vapor deposition batch process synthesis of carbon nanotube system. The authors concluded that NiO/CuO produced higher CNT yields and had a good arrangement structure. The CuO/CoO catalyst system produces amorphous carbon. Compared with the single metal catalyst system, the bimetal catalyst composition has higher performance and well-aligned carbon nanotubes.

Alloying of catalyst

Catalyst metal alloys have shown a significant effect on single-phase metals. The author revealed that catalyst alloys enhance the decomposition of carbon sources; in addition,

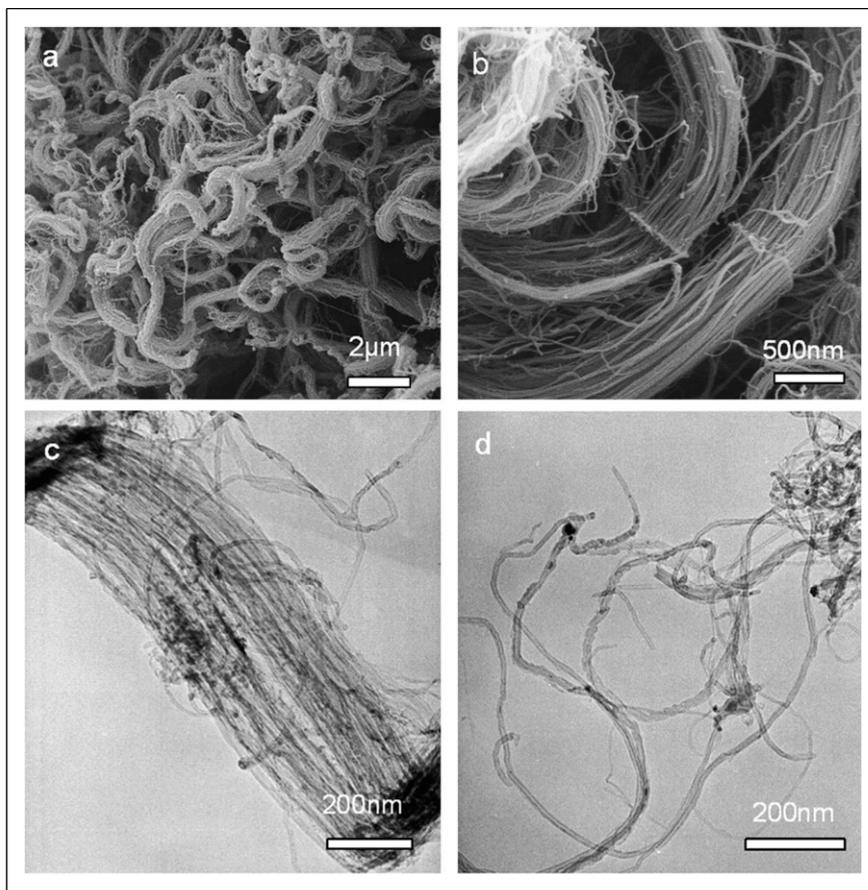


Figure 9. Electron microscopy image of typical product synthesized under the optimal reaction conditions: (a and b) SEM images; (c and d) TEM images (Zhan et al., (2007)).⁴⁷

Table 3. Solubility and carbon diffusion coefficients of catalyst metals (Lamouroux et al., (2007)).⁵⁵

Properties	Fe	Co	Ni
Carbon solubility at melting point (at %)	20.2	13.9	10.7
Carbon diffusion coefficient at 1000°C ($\text{m}^2 \text{s}^{-1}$)	1.5×10^{-11}	1×10^{-11}	2×10^{-11}

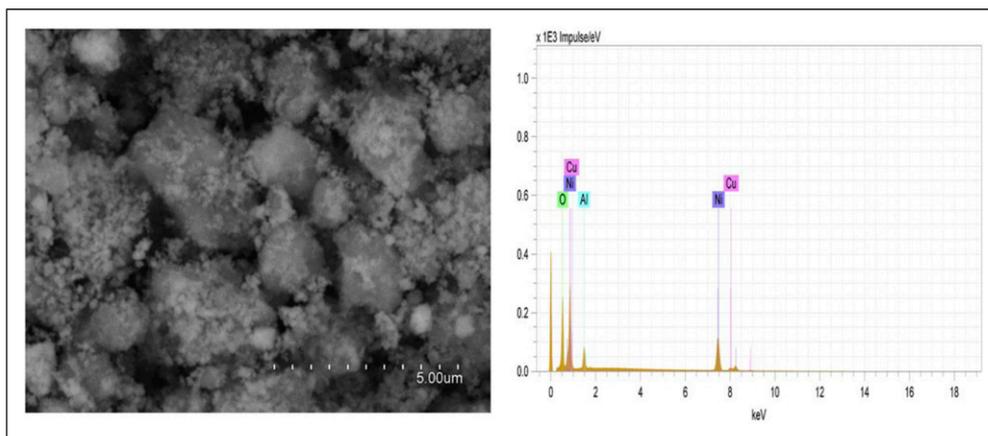


Figure 10. SEM image and EDX analysis of the NiCu/Al₂O₃ catalyst (Pinilla et al., (2000)).²⁹

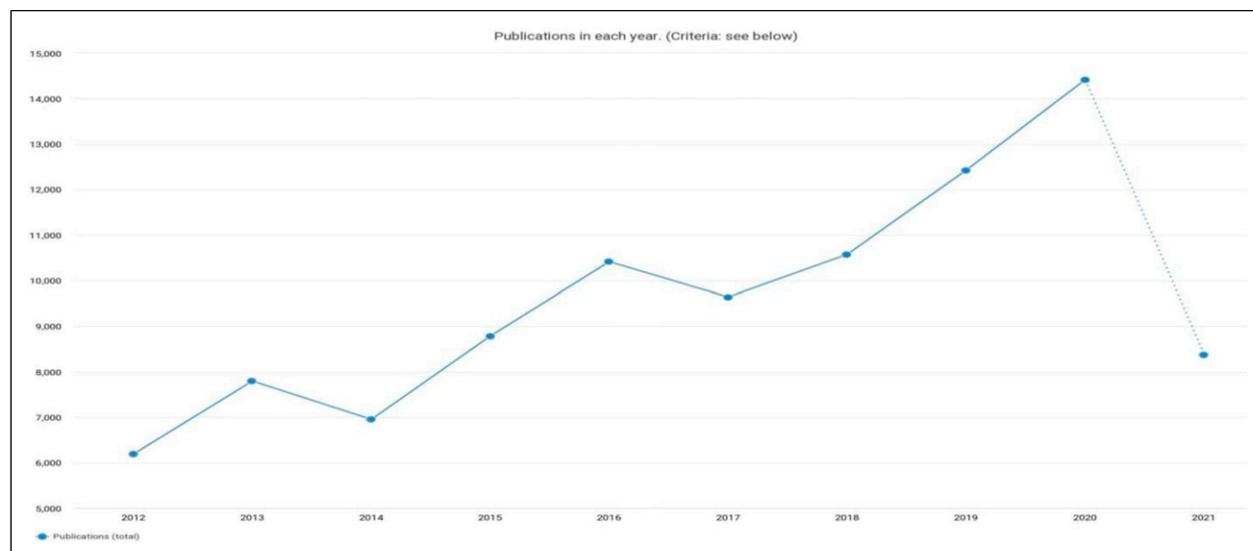


Figure 11. Articles published in CNTs synthesis from the year 2012–2020 (<https://www.dimensions.ai/>).

Table 4. Researchers published paper in CNTs from 2012 to 2021 (<https://www.dimensions.ai/>).

S.No	Name Organization, country	Publications	Citations	Citations mean
1	Pulickel Madhavapanicker Ajayan Rice university, United States	186	17,298	93.00
2	Yoshio Bando National Institute for Materials Science, Japan	172	14,690	85.41
3	Mauricio Terrones Pennsylvania State University, United States	168	13,732	81.74
4	Dmitri V Golberg Queensland University of Technology, Australia	165	12,413	75.23
5	Fei Wei Tsinghua university, China	159	13,194	82.98
6	Kostya Ken Ostrikov Queensland University of Technology, Australia	146	5576	38.19
7	Ahmad Fauzi Ismail University of Technology Malaysia, Malaysia	143	5400	37.76
8	Hui-Ming Cheng Institute of Metals Research, China	143	24,446	170.95
9	Seeram Ramakrishna National University of Singapore, Singapore	142	14,686	103.42
10	Qiang Zhang Tsinghua University, China	140	14,486	103.47

alloys can also affect carbon supply and diffusion in many ways:

1. The melting temperature of binary (or higher) catalysts is usually lower than that of a single metal, resulting in carbon higher solubility in the catalyst
2. The synergistic effect can be attributed to the reorganization of the metal lattice structure, for example, by changing the vacancy and spacing of the crystal

plane, which can improve the diffusion and transport of carbon atoms through the bulk metal catalyst.

3. Additional elements can reduce the binding energy of the catalyst metal and carbon atoms, thereby improving the diffusibility.⁵²

Impact of CNTs research

Figure 11 shows the schematic representation of articles published in CNTs from the year 2012 to 2020. The data is

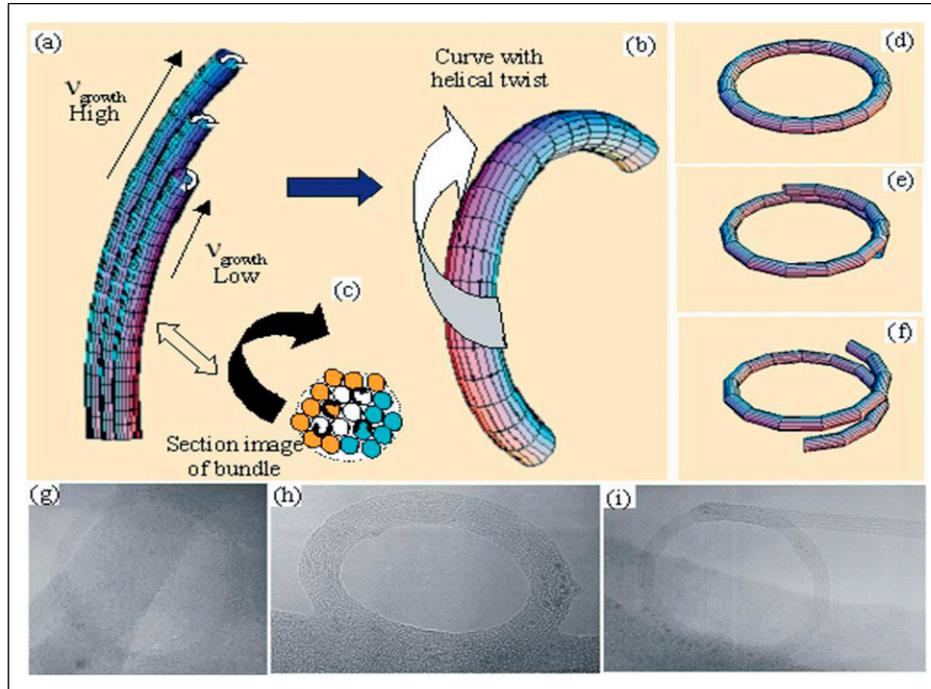


Figure 12. Schematic representation of the growth mechanism of carbon rings. The cylinder corresponds to a SWNT bundle. **a, b)** The bundles are induced to twist and bend by the varying growth stress for different nanotubes and due to the tube–tube interactions. **c)** Schematic representation of a cross section of SWNT bundles showing the varying growth rates of the nanotubes and the SWNTs twisting against one another. **d–f)** Possible shapes of bundles resulting from the curling process, compared with **g–i)** TEM images of SWNT rings observed in the experiments (Song, et. al., (2006)).¹⁹

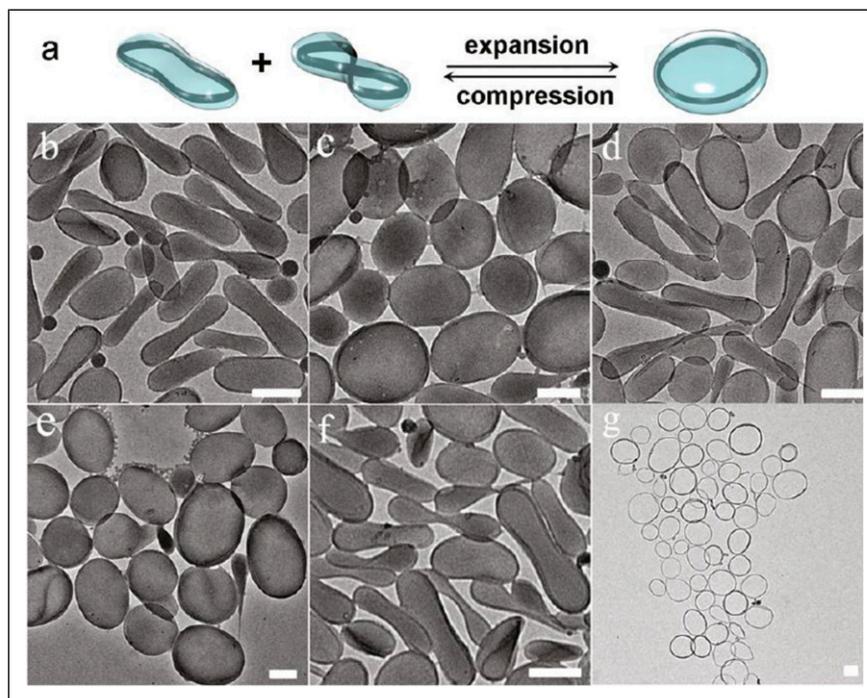


Figure 13. (a) Schematic representation and (b to g) TEM images of carbon nanorings undergoing five consecutive steps of structural transformation. Compressed rings (b) were expanded to circular rings (c) by moderate swelling of their shells. They were compressed again (d), expanded again (e), compressed again (f), and then finally expanded by dissolving away their polymer shells (g). All scale bars represent 200 nm (Cheng, et. al., (2011)).⁵⁸

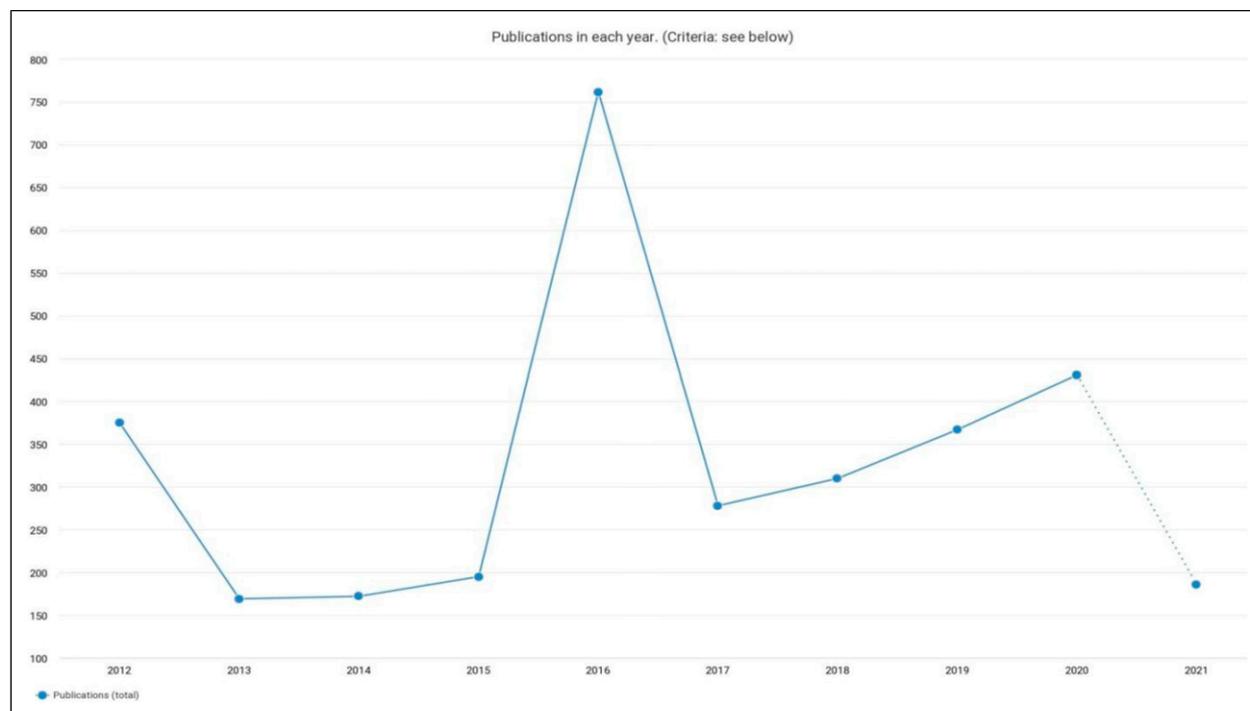


Figure 14. Articles published in CNRs synthesis from the year 2012–2020 (<https://www.dimensions.ai/>).

Table 5. Researchers published paper in CNRs from 2012 to 2021 [<https://www.dimensions.ai/>].

S.No	Name Organization, country	Publications	Citations	Citations mean
1	Ramanathan Chandiramouli SASTRA University, India	40	547	13.68
2	Veerappan Nagarajan SASTRA University, India	39	532	13.64
3	Zhong Lin Wang Georgia Institute of Technology, United States	38	15,773	415.08
4	Kenichiro Itami Nagoya University, Japan	37	3465	93.65
5	Yasutomo Segawa Nagoya University, Japan	30	3162	105.40
6	Guo-Xiu Tong Zhejiang Normal University, China	28	1006	35.93
7	Xifang Chen Joint Laboratory for Extreme Conditions Matter Properties, China	26	1165	44.81
8	Lai-Fei Cheng Northwestern Polytechnical University, China	26	1169	44.96
9	Edmond Gravel University of Paris-Saclay, France	25	823	32.92
10	You-Gen Yi Central South University, China	25	1067	42.68

obtained from the diemensions.ai. From [Figure 11](#), it was clearly understood that the articles published in CNTs synthesis were kept on increasing by year by year. This graph represents the CNTs synthesized using the CVD process, this shows the importance CVD process for

industrial scale-up. Also, [Table 4](#) shows the top 10 researchers who published articles in CNTs synthesis for the past decade. [Table 4](#) is composed of the name of the researcher and their respective affiliation, the number of publications, citations, and citation mean.

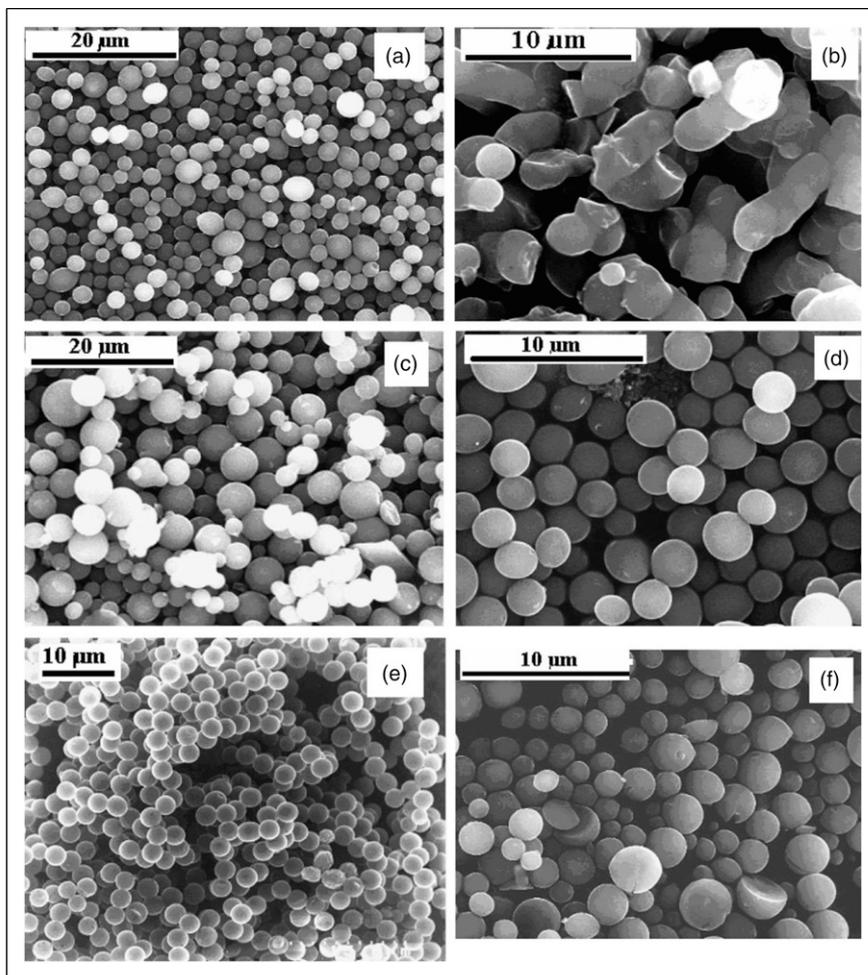


Figure 15. SEM image of (a) pentane, (b) cyclohexane, (c) camphorquinone, (d) xylene, (e) mesitylene, and (f) camphene (Pol. et al., (2006)).⁶⁵

Carbon nanorings

Due to the research carried out on carbon nanotubes (CNTs), especially the synthesis of different allotropes of carbon nanomaterials, such as carbon nanorings,⁵⁶ carbon nanorods,⁵⁷ and carbon nanospheres.⁵⁸ Nanotechnology field is becoming more and more obvious. After CNTs, single-walled carbon nanorings (SWCNRs) and multi-walled carbon nanorings (MWCNRs) have been found to be the most interesting carbon nanostructures because they are considered the giants of all carbon structures and are used directly as nanoscale devices.⁸ Recently, several research groups have reported the formation of modified CNTs in toroidal carbon tubes through post-treatment processes.^{35,56,59} In most cases, the post-treatment process involves a chemical treatment to fold the CNT into a ring structure, which can change the basic properties of the nanotubes.⁶⁰

Zhou. et al. 2006,⁶¹ synthesized SWCNRs in a floating catalyst chemical vapor deposition (FCCVD) process. FCCVD consists of a dual furnace configuration in, which

the catalyst is placed in the first furnace and the substrate was placed in the second furnace at 1100°C. Song. et al., (2006)¹⁹ used the FCCVD process and ferrocene as a catalyst, SWCNRs was synthesized in a similar way at 1100° C. However, few investigators report the use of catalytic CVD^{56,58,62,63} to synthesize CNRs. There is a lack of information on the characteristics of the catalyst particles that were used to synthesize CNRs, especially in the catalytic chemical vapor deposition (CCVD) process.

Recently, Venkatesan. et al., (2018)⁶⁴ optimized the CCVD parameters to synthesize well-aligned multi-walled carbon nanotubes (MWCNTs) using Ni/Al₂O₃ as a catalyst material. It is believed, that CNT bundles can be grow abundantly using agglomerated catalyst particles.

Effect of CVD process parameters on CNRs growth

There is no much study reported on the effect of CVD process parameters on the structure of CNRs. Song. et al., (2006)¹⁹ synthesized CNRs using the CVD process. The

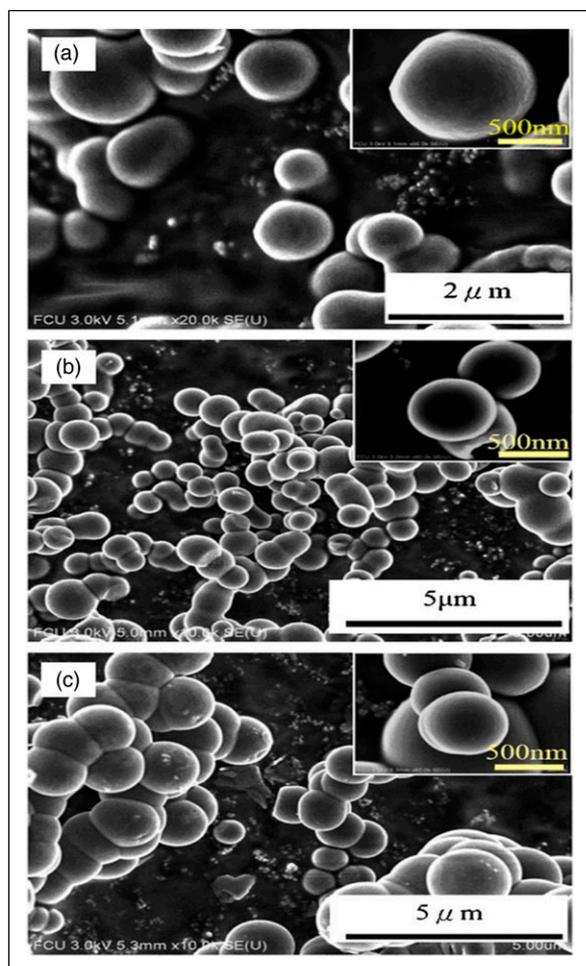


Figure 16. SEM images of (a) CS-La, (b) CS-Nb, and (c) CS-Ti; all synthesized at 720°C. The insets are enlarged portions (Lee, et. al., (2011))³⁸.

author studied the growth process with respect to the experimental parameters to obtain optimal synthesis conditions. SWNT rings amount of growth was determined by the amount of sublimation catalyst, which can be adjusted by changing the sublimation temperature, with an increase in the sublimation temperature from 50 to 65°C, more of the catalyst is sublimed; and the samples tend to have proportionately more SWNTs with linear structure. Conversely, when the sublimation temperature is below 50°C, neither ring nor linear SWNT products are obtained. Meanwhile, author has been found that the reactant gas flow greatly influences the formation of SWNT rings. The optimum flow ranges from 200 to 600 sccm with the ratio of acetylene to argon varying from about 0.02 to 0.1 vol % (See Figure 12). Further, they found that the quantity of SWNT rings obtained is also influenced by other experimental parameters, such as the reaction time and the growth temperature. Therefore, by adjusting these parameters, one can deposit

SWNT rings onto different substrates with a wide range of densities, as demonstrated in Figure 12.

Chen, et. al. (2011)⁵⁸ used molecular dynamics (MD) simulation methods to study thermal stability and morphological changes of nanorings with different radii during temperature increase. Using the different initial C-C bond lengths of the chair carbon nanotubes, five metastable nanorings were generated. The stable structure of the two smallest nanorings has several twisted regions around the nanorings, and the deformation of the inner and outer walls occurs at the same temperature. For the three largest cases, the morphology of the nanoring in the top view shows a circle at 0 K. For a nanoring with a radius of 146 Å (350 units), the thermal deformation process is very similar to the two smaller cases. However, the temperature at which the thermal deformation starts is higher.

For the nanoring with ring radii of 165 Å (400 units) and 185 Å (450 units), the inner wall of the nanoring will be thermally deformed, and then the outer wall will be deformed at higher temperatures. Figure 13 shows the changes of the local structure of the distorted area at different temperatures.

Impact of CNRs research

Figure 14 shows the schematic representation of articles published in CNRs from the year 2012 to 2020. The data are obtained from the dimensions.ai. From Figure 14, it was clearly understood that the articles published in CNTs synthesis were drops after the year 2016. Also, Table 5 shows the top 10 researchers who published articles in CNRs synthesis for the past decade. Table 5 is composed of the name of the researcher and their respective affiliation, the number of publications, citations, and citation mean.

Carbon nanospheres

Zhang et. al. 2016²⁰ synthesized CNSs using a non-catalytic CVD process and reported the formation mechanism using CH₄ and H₂ as the precursor gas. Xu et. al. (2005)¹⁶ synthesized CNSs using two different substrates such as kaolin-supported catalyst and ceramic plate via CVD process using C₂H₂ and reported that they synthesized two different kinds of carbon nanostructures, carbon nanotubes, and carbon spheres. Li et. al., (2016)³⁸ synthesized hollow carbon spheres and yolk-structured carbon spheres using metal catalyst-free CVD process using methane as the precursor gas.

Effect of CVD process parameters on CNSs

Zhang, et. al. (2016)²⁰ synthesized CNSs by non-catalytic chemical vapor deposition of natural gas/hydrogen mixtures. Author varied the deposition temperature from 1070 to 1200°C, the deposition temperature showed no significant effect on the sphere size and structure. The author

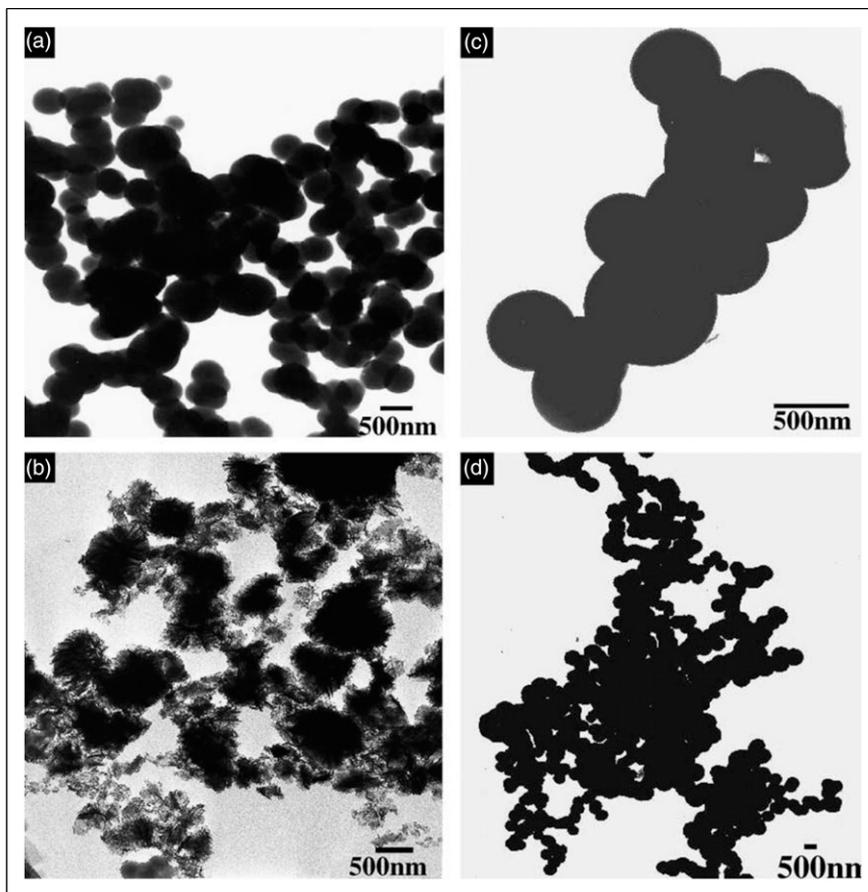


Figure 17. TEM images of the carbon spheres treated by different chemicals: (a) carbon spheres in HF (48%) solution for 48 h at 25°C, (b) carbon spheres in KMnO₄ (H₂) solution for 2 h at 80°C, (c) in CS₂ for 10 h and (d) in 1-methyl-naphthalene for 10 h (Miao. et. al., (2004)).⁶⁶

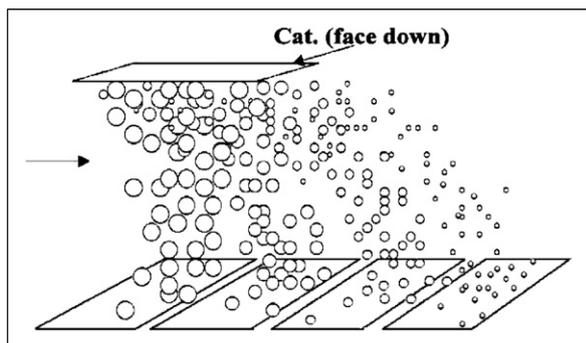


Figure 18. The schematic representation shows the entire process of preparation, purification and isolation of carbon spheres (Miao. et. al., (2004)).⁶⁶

revealed that with the increase of deposition pressure, the chance of collision of carbon sphere nuclei was increased. Hydrogen was likely to adsorb to the surface of carbon sphere nuclei and reduce the collision probability of carbon sphere nuclei. It was revealed that carbon nanospheres (50–

100 nm) could be produced at 1150°C and 5 kPa with a gas mixture of natural gas/H₂=1/4.

Pol. et. al. (2006)⁶⁵ studied various hydrocarbons containing 5–14 carbon atoms (pentane, cyclohexane, camphorquinone, xylene, mesitylene, camphene, decahydronaphthalene, diphenylmethane, and anthracene) were dissociate under their autogenic pressure developed at 700°C to produce pure carbon materials (see Figure 15). From all of the hydrocarbons, more than 99% pure carbon is obtained in spherical, filament- or egg-like microstructures.

The key thing in the thermal dissociation of various hydrocarbons, followed by solidification under autogenic pressure, is the shape of products with micrometer dimensions, while the organometallic compounds yield nanometric products via a similar method. Specific systematic morphological, structural, and compositional analysis is presented for the products obtained from the thermal dissociation of diphenylmethane. Lee. et. al., (2011)³⁸ synthesized sub-micrometer carbon spheres successfully by catalytic CVD using novel catalyst on kaolin support. The author claiming that they reported for the first time that the non-magnetic metal (La, Nb, and Ti)

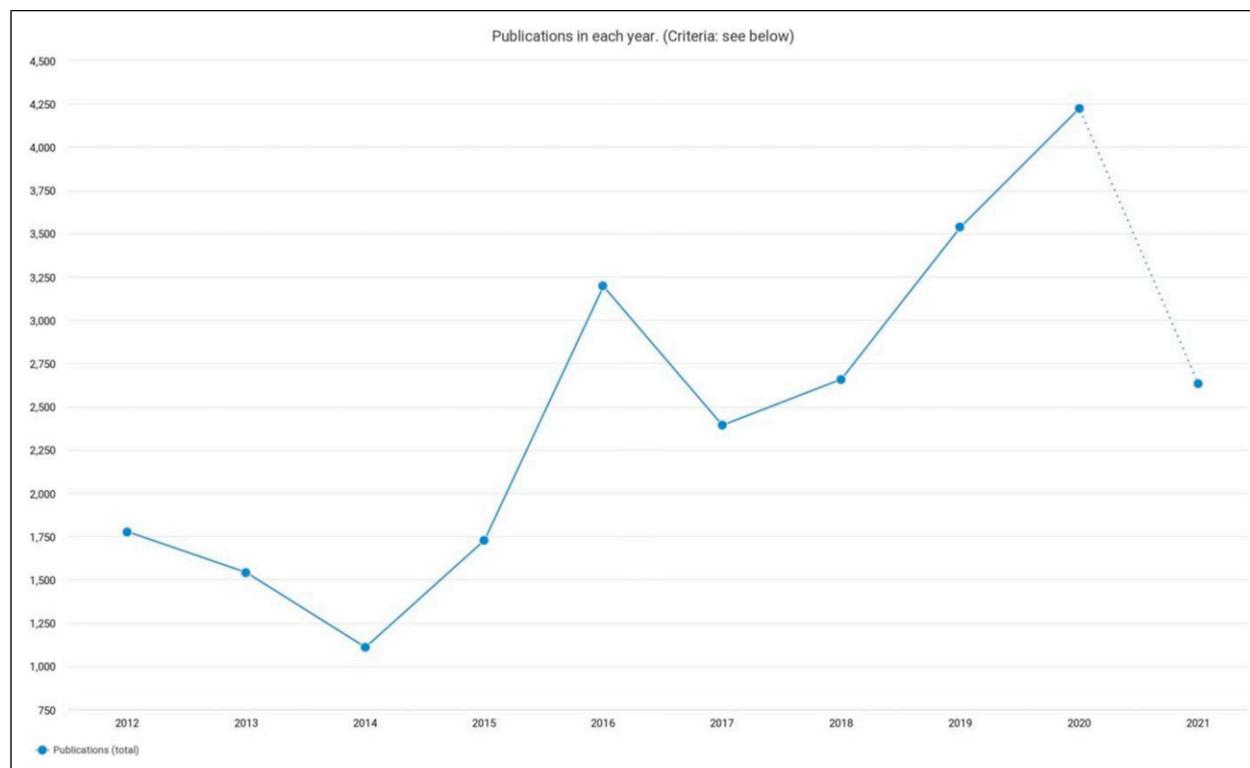


Figure 19. Articles published in CNSs from the year 2012–2020 (<https://www.dimensions.ai/>).

complexes catalyzed the carbonization of C_2H_2 into carbon spheres. The author reveals that the favorable growth temperature falls between 720 and 810 C. The X-ray diffraction patterns of carbon spheres show graphitic structure with transition metal crystallites excluded. The diameters of solid-core carbon spheres using La, Nb, and Ti as catalyst were determined by TEM as 600–875, 425–1100, and 650–1250 nm, respectively (see Figure 16). The acquired curves of magnetic susceptibility for Carbon spheres show background noises only, indicating no superconductivity and encapsulation of transition metal nanoparticles. The Raman spectra at room temperature showed a higher degree of graphitization for the La-catalyzed carbon spheres, based on the relative intensity of the feature peaks at 1325 cm^{-1} and 1580 cm^{-1} . Finally, the author concluded that the CS-Ti and CS-La are two promising candidates for traditional and novel applications due to their comparable thermal and electrical conductivity to those of commercial carbon black.

Miao. et. al., (2004)⁶⁶ synthesized carbon spheres with diameters in the range 400–2000 nm are by catalytic CVD in large quantities using kaolin-supported cobalt catalysts (see Figure 17). Using this technique, one can optimize the size of the carbon spheres with the conditions of their report and with high yields produced within the temperature range 750–850°C

The Dysonian shape of ESR spectra indicates metallic nature for the carbon nanostructure. ESR and SQUID measurements indicate the existence of significant magnetization

and indicate the possibility of using these materials for commercial magnetic applications. The highly inert and lightweight mechanical properties of these spheres give hope that they may be promising as lightweight materials for spacecraft applications. The author has depicted the entire synthesized step as a schematic representation as shown in Figure 18.

Impact of CNSs research

Figure 19 shows the schematic representation of articles published in CNSs from the year 2012 to 2020. The data are obtained from the dimensions.ai. From Figure 19, it was clearly understood that the articles published in carbon spheres were increasing after the year 2016. Also, Table 6 shows the top 10 researchers who have published articles in CNSs for the past decade. Table 6 is composed of the name of the researcher and their respective affiliation, the number of publications, citations, and citation mean.

Summary and future scope

“Buckytubes are in high school now,” statement said by Rick Smalley, in 2000. After 20 years of research, researchers have discovered many allotropies of carbon like sphere and ring structures. The growth mechanisms of the CNTs were clearly understood from the literature survey. But the growth mechanisms of the spheres and rings were

Table 6. Researchers published paper in CNSs from 2012 to 2021 (<https://www.dimensions.ai/>).

S.No	Name Organization, country	Publications	Citations	Citations mean
1	Huan Pang Yangzhou University, China	53	3665	69.15
2	Seeram Ramakrishna National University of Singapore, Singapore	42	2169	51.64
3	Han Zhang Shenzhen University, China	39	1558	39.95
4	Karin Cenzual University of Geneva, Switzerland	37	0	-
5	Bharat Bhushan The Ohio State University, United States	36	1898	52.72
6	Yusuke Yamauchi University of Queensland, Australia	35	3777	107.91
7	Huai-Guo Xue Yangzhou University, China	33	3243	98.27
8	Shi Xue Dou University of Wollongong, Australia	33	2054	62.24
9	Ki-Hyun Kim Hanyang University, South Korea	32	1284	40.13
10	Li-Qiang Mai Wuhan University of Technology, China	29	2470	85.17

still in debate. The impact of research in allotropies of carbon nanostructures reveals that the publication of articles in rings and spheres (see Figures 14 and 19) drastically decreased after 2016. But articles published on CNTs research keep on increasing, which is seen from Figure 11. Researchers also claim that the CVD process was a viable technique to synthesis CNTs as compared to other synthesizing techniques like arc discharge and laser ablation. Many researchers have controlled the morphology of the CNTs like diameter and length. Authors also used statistical tools like response surface methodology to optimize the CVD process parameters to control the chemical and physical structure of CNTs.^{67,68} Researchers also have optimized the CVD process parameters to increase the yield of the CNTs to use the CVD on an industrial scale. Catalysis is the seed of the CVD–CNT technique and it seems that researchers have used many transition metals to grow CNTs in the CVD process. Researchers have used transition metal catalysts like Ni, Cu, Co, Fe, and Al to grow CNTs via the CVD process. CNTs were successfully used in applications like hydrogen storage, electron emission, and drug delivery, reinforcement for composites.^{69,70,71} On the other hand, there is no much research was undertaken in synthesizing spheres and rings. But spheres and rings are capable of performing better than CNTs structure in energy storage, and sensors.

Acknowledgements

The first author gratefully acknowledges the financial support provided by M/s. VB Ceramics Consultants (VBCC), Nehru Nagar Industrial Estate, Kottivakkam, Chennai-600041, and India

through VBCRF (VBCERAMICS RESEARCH FELLOWSHIP). The first author grateful to the Dr K. Suresh Babu, Assistant Professor, Centre for Nano Sciences and Technology, Madanjeet School of Green Energy Technologies, Pondicherry University, for his fruitful discussions.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) received no financial support for the research, authorship, and/or publication of this article.

ORCID iD

Sivamaran V  <https://orcid.org/0000-0001-9245-0022>

References

1. Monthieux M, Serp P, Caussat B, et al. *Carbon Nanotubes*. Springer Handbooks, 2017, pp. 193–247. DOI: [10.1007/978-3-662-54357-3_8](https://doi.org/10.1007/978-3-662-54357-3_8).
2. Basiuk EV, Ramirez-Calera IJ, Meza-Laguna V, et al. Solvent-free functionalization of carbon nanotube buckypaper with amines. *Appl Surface Science* 2015; 357: 1355–1368, doi:[10.1016/j.apsusc.2015.09.252](https://doi.org/10.1016/j.apsusc.2015.09.252).
3. Ijimia S. Helical microtubules of graphitic carbon. *Lett Nat* 1991; 354: 56–57.
4. Peng B, Locascio M, Zapol P, et al. Measurements of near-ultimate strength for multiwalled carbon nanotubes and

- irradiation-induced crosslinking improvements. *Nat Nanotechnology* 2008; 3: 626–631. DOI: [10.1038/nnano.2008.211](https://doi.org/10.1038/nnano.2008.211).
5. Liu X, Guo R, Lin Z, et al. Resistance-strain sensitive rubber composites filled by multiwalled carbon nanotubes for structural deformation monitoring. *Nanomater Nanotechnology* 2021; 11: 184798042110113. DOI: [10.1177/18479804211011384](https://doi.org/10.1177/18479804211011384).
 6. De Volder MF, Tawfik SH, Baughman RH, et al. Carbon nanotubes: present and future commercial applications. *Science* 2013; 339(80): 535–539. DOI: [10.1126/science.1222453](https://doi.org/10.1126/science.1222453).
 7. Ismail N, Jalar A, Afdzaluddin A, et al. Electrical resistivity of Sn-3.0Ag-0.5Cu solder joint with the incorporation of carbon nanotubes. *Nanomater Nanotechnology* 2021; 11: 1847980421996539. DOI: [10.1177/1847980421996539](https://doi.org/10.1177/1847980421996539).
 8. Liu L, Liu F, and Zhao J. Curved carbon nanotubes: from unique geometries to novel properties and peculiar applications. *Nano Res* 2014; 7: 626–657. DOI: [10.1007/s12274-014-0431-1](https://doi.org/10.1007/s12274-014-0431-1).
 9. Liu J, Wickramaratne NP, Qiao SZ, et al. Molecular-based design and emerging applications of nanoporous carbon spheres. *Nat Mater* 2015; 14: 763–774. DOI: [10.1038/nmat4317](https://doi.org/10.1038/nmat4317).
 10. Tang K, Fu L, White RJ, et al. Hollow carbon nanospheres with superior rate capability for sodium-based batteries. *Adv Energy Mater* 2012; 2: 873–877. DOI: [10.1002/aenm.201100691](https://doi.org/10.1002/aenm.201100691).
 11. You B, Yang J, Sun Y, et al. Easy synthesis of hollow core, bimodal mesoporous shell carbon nanospheres and their application in supercapacitor. *Chem Commun* 2011; 47: 12364–12366. DOI: [10.1039/c1cc15348j](https://doi.org/10.1039/c1cc15348j).
 12. Zhang WM, Hu JS, Guo YG, et al. Tin-nanoparticles encapsulated in elastic hollow carbon spheres for high-performance anode material in lithium-ion batteries. *Adv Mater* 2008; 20: 1160–1165. DOI: [10.1002/adma.200701364](https://doi.org/10.1002/adma.200701364).
 13. Zhang K, Zhao Q, Tao Z, et al. Composite of sulfur impregnated in porous hollow carbon spheres as the cathode of Li-S batteries with high performance. *Nano Res* 2013; 6: 38–46. DOI: [10.1007/s12274-012-0279-1](https://doi.org/10.1007/s12274-012-0279-1).
 14. Zhao Y, Li J, Wu C, et al. A yolk-shell Fe₃O₄@C composite as an anode material for high-rate lithium batteries. *Chempluschem* 2012; 77: 748–751.
 15. Zheng G, Lee SW, Liang Z, et al. Interconnected hollow carbon nanospheres for stable lithium metal anodes. *Nat Nanotechnol* 2014; 9: 618–623. DOI: [10.1038/nnano.2014.152](https://doi.org/10.1038/nnano.2014.152).
 16. Xu ZX, Lin JD, Roy VAL, et al. Catalytic synthesis of carbon nanotubes and carbon spheres using kaolin supported catalyst. *Mater Sci Eng B* 2005; 123: 102–106. DOI: [10.1016/j.mseb.2005.07.012](https://doi.org/10.1016/j.mseb.2005.07.012).
 17. Eatemadi A, Daraee H, Karimkhanloo H, et al. Carbon nanotubes: properties, synthesis, purification, and medical applications. *Nanoscale Res Lett* 2014; 9: 393–413. DOI: [10.1186/1556-276X-9-393](https://doi.org/10.1186/1556-276X-9-393).
 18. Plonska-Brzezinska ME. Carbon nano-onions: a review of recent progress in synthesis and applications. *Chem Nano Mat*. 2019; 5: 568–580. DOI: [10.1002/cnma.201800583](https://doi.org/10.1002/cnma.201800583).
 19. Song L, Ci LJ, Sun LF, et al. Large-scale synthesis of rings of bundled single-walled carbon nanotubes by floating chemical vapor deposition. *Adv Mater* 2006; 18: 1817–1821. DOI: [10.1002/adma.200502372](https://doi.org/10.1002/adma.200502372).
 20. Zhang Y, Yang W, Luo RY, et al. Preparation of carbon nanospheres by non-catalytic chemical vapor deposition and their formation mechanism. *New Carbon Mater* 2016; 31: 467–474. DOI: [10.1016/S1872-5805\(16\)60025-2](https://doi.org/10.1016/S1872-5805(16)60025-2).
 21. Dresselhaus MS, *Carbon nanotubes*. SPIN Springer's internal project number. 2000, pp. 463.
 22. Das S. A review on carbon nano-tubes - a new era of nanotechnology. *Int J Emerging Technology Adv Eng* 2013; 3(Issue 3): 774–783.
 23. Nourbakhsh A, Ganjipour B, Zahedifar M, et al. Morphology optimization of CCVD-synthesized multiwall carbon nanotubes, using statistical design of experiments. *Nanotechnology* 2007; 18: 115715. DOI: [10.1088/0957-4484/18/11/115715](https://doi.org/10.1088/0957-4484/18/11/115715).
 24. Kumar M and Ando Y. Chemical vapor deposition of carbon nanotubes: a review on growth mechanism and mass production. *J Nanosci Nanotechnol* 2010; 10: 3739–3758. DOI: [10.1166/jnn.2010.2939](https://doi.org/10.1166/jnn.2010.2939).
 25. Sivakumar VM, Abdullah AZ, Mohamed AR, et al. Optimized parameters for carbon nanotubes synthesis over Fe and Ni catalysts VIA methane CVD. *Rev Adv Mater Sci* 2011; 27: 25–30.
 26. Awadallah AE, Abdel-Hamid SM, El-Desouki DS, et al. Synthesis of carbon nanotubes by CCVD of natural gas using hydrotreating catalysts. *J Pet* 2012; 21: 101–107. DOI: [10.1016/j.ejpe.2012.11.005](https://doi.org/10.1016/j.ejpe.2012.11.005).
 27. Tyagi PK, Janowska I, Cretu O, et al. Catalytic action of gold and copper crystals in the growth of carbon nanotubes. *J Nanosci Nanotechnol* 2011; 11: 3609–3615. DOI: [10.1166/jnn.2011.3740](https://doi.org/10.1166/jnn.2011.3740).
 28. Kruszka B, Terzyk AP, Wiśniewski M, et al. Synthesis of carbon nanotubes and nanotube forests on copper catalyst. *Mater Res Express* 2014; 1: 035040. DOI: [10.1088/2053-1591/1/3/035040](https://doi.org/10.1088/2053-1591/1/3/035040).
 29. Pinilla JL, Suelves I, Lázaro MJ, et al. Parametric study of the decomposition of methane using a NiCu/Al₂O₃ catalyst in a fluidized bed reactor. *Int J Hydrogen Energy* 2010; 35: 9801–9809. DOI: [10.1016/j.ijhydene.2009.10.008](https://doi.org/10.1016/j.ijhydene.2009.10.008).
 30. Ch Das N, Yang K, Liu Y, et al. Quantitative characterization of vertically aligned multi-walled carbon nanotube arrays using small angle x-ray scattering. *J Nanosci Nanotechnol* 2011; 11: 4995–5000. DOI: [10.1166/jnn.2011.4110](https://doi.org/10.1166/jnn.2011.4110).
 31. Atthipalli G, Epur R, Kumta PN, et al. The effect of temperature on the growth of carbon nanotubes on copper foil using a nickel thin film as catalyst. *Thin Solid Films* 2011; 519: 5371–5375. DOI: [10.1016/j.tsf.2011.02.046](https://doi.org/10.1016/j.tsf.2011.02.046).
 32. Tripathi N, Mishra P, Harsh H, et al. Fine-tuning control on CNT diameter distribution, length and density using thermal

- CVD growth at atmospheric pressure: an in-depth analysis on the role of flow rate and flow duration of acetylene (C₂H₂) gas. *Appl Nanosci* 2015; 5: 19–28. DOI: [10.1007/s13204-013-0288-8](https://doi.org/10.1007/s13204-013-0288-8).
33. Fathy NA. Carbon nanotubes synthesis using carbonization of pretreated rice straw through chemical vapor deposition of camphor. *RSC Adv* 2017; 7: 28535–28541. DOI: [10.1039/c7ra04882c](https://doi.org/10.1039/c7ra04882c).
 34. Ahmad S, Liao Y, Hussain A, et al. Systematic investigation of the catalyst composition effects on single-walled carbon nanotubes synthesis in floating-catalyst CVD. *Carbon N Y* 2019; 149: 318–327. DOI: [10.1016/j.carbon.2019.04.026](https://doi.org/10.1016/j.carbon.2019.04.026).
 35. Sun J, Liu H, Chen X, et al. Carbon nanorings and their enhanced lithium storage properties. *Adv Mater* 2013; 25: 1125–1130. DOI: [10.1002/adma.201203108](https://doi.org/10.1002/adma.201203108).
 36. Wang W, Laird ED, Gogotsi Y, et al. Bending single-walled carbon nanotubes into nanorings using a Pickering emulsion-based process. *Carbon* 2012; 50: 1769–1775. DOI: [10.1016/j.carbon.2011.12.024](https://doi.org/10.1016/j.carbon.2011.12.024).
 37. Lei CM, Yuan WL, Huang HC, et al. Synthesis and conductivity measurement of carbon spheres by catalytic CVD using non-magnetic metal complexes. *Synth Met* 2011; 161: 1590–1595. DOI: [10.1016/j.synthmet.2011.05.023](https://doi.org/10.1016/j.synthmet.2011.05.023).
 38. Li X, Chi M, Mahurin SM, et al. Graphitized hollow carbon spheres and yolk-structured carbon spheres fabricated by metal-catalyst-free chemical vapor deposition. *Carbon* 2016; 101: 57–61. DOI: [10.1016/j.carbon.2016.01.043](https://doi.org/10.1016/j.carbon.2016.01.043).
 39. Qu L, Zhang H, Zhu J, et al. Tunable assembly of carbon nanospheres on single-walled carbon nanotubes. *Nanotechnology* 2010; 21: 305602. DOI: [10.1088/0957-4484/21/30/305602](https://doi.org/10.1088/0957-4484/21/30/305602).
 40. Gonzalez-Reyna M, Rodriguez-Lopez A, and Pérez-Robles JF. One-step synthesis of carbon nanospheres with an encapsulated iron-nickel nanoalloy and its potential use as an electrocatalyst. *Nanotechnology* 2020; 32: 095706.
 41. Qu L, Zhang H, Zhu J, et al. Tunable assembly of carbon nanospheres on single-walled carbon nanotubes. *Nanotechnology* 2010; 21(8pp): 305602. DOI: [10.1088/0957-4484/21/30/305602](https://doi.org/10.1088/0957-4484/21/30/305602).
 42. Pant M, Singh R, Negi R, et al. A comprehensive review on carbon nano-tube synthesis using chemical vapor deposition. *Mater Today Proc* 2021; 46: 11250–11253. DOI: [10.1016/j.matpr.2021.02.646](https://doi.org/10.1016/j.matpr.2021.02.646).
 43. Baker R, Barber MA, Harris PS, et al. Nucleation and growth of carbon deposits from the nickel catalyzed decomposition of acetylene. *J Catal* 1972; 26: 51–62. DOI: [10.1016/0021-9517\(72\)90032-2](https://doi.org/10.1016/0021-9517(72)90032-2).
 44. Yan Y, Miao J, Yang Z, et al. Carbon nanotube catalysts: recent advances in synthesis, characterization and applications. *Chem Soc Rev* 2015; 44: 3295–3346. DOI: [10.1039/c4cs00492b](https://doi.org/10.1039/c4cs00492b).
 45. He CN, Zhao NQ, Shi CS, et al. An approach for obtaining the structural diversity of multi-walled carbon nanotubes on Ni/Al catalyst with low Ni content. *J Alloys Compd* 2010; 489: 20–25. DOI: [10.1016/j.jallcom.2009.09.067](https://doi.org/10.1016/j.jallcom.2009.09.067).
 46. Shukrullah S, Mohamed NM, Shaharun MS, et al. Effect of ethylene flow rate and CVD process time on diameter distribution of MWCNTs. *Mater Manuf Process* 2016; 31: 1537–1542. DOI: [10.1080/10426914.2015.1090588](https://doi.org/10.1080/10426914.2015.1090588).
 47. Zhan S, Tian Y, Cui Y, et al. Effect of process conditions on the synthesis of carbon nanotubes by catalytic decomposition of methane. *China Particuology* 2007; 5: 213–219. DOI: [10.1016/j.cpart.2007.03.004](https://doi.org/10.1016/j.cpart.2007.03.004).
 48. Hernadi K, Fonseca A, Nagy JB, et al. Production of nanotubes by the catalytic decomposition of different carbon-containing compounds. *Appl Catal A Gen* 2000; 199: 245–255. DOI: [10.1016/S0926-860X\(99\)00561-X](https://doi.org/10.1016/S0926-860X(99)00561-X).
 49. Qian W, Yu H, Wei F, et al. Synthesis of carbon nanotubes from liquefied petroleum gas containing sulfur. *Carbon* 2002; 40: 2968–2970. DOI: [10.1016/S0008-6223\(02\)00244-0](https://doi.org/10.1016/S0008-6223(02)00244-0).
 50. Shin KY, Su HC, and Tsai CH. In situ growth of single-walled carbon nanotubes by bimetallic technique with/without dielectric support for nanodevice applications. *J Vac Sci Technol B Microelectron Nanom Struct* 2006; 24: 358. DOI: [10.1116/1.2151223](https://doi.org/10.1116/1.2151223).
 51. Mendoza MP, Valles C, Maser WK, et al. 2005.
 52. Li Y, Chen J, and Chang L. Catalytic growth of carbon fibers from methane on a nickel-alumina composite catalyst prepared from feitknecht compound precursor. *Appl Catal A Gen* 1997; 163: 45–57. DOI: [10.1016/S0926-860X\(97\)00116-6](https://doi.org/10.1016/S0926-860X(97)00116-6).
 53. Shlyakhova EV, Yudanov NF, Shubin YV, et al. Catalytic synthesis of carbon nanotubes using Ni- and Co-doped calcium tartrates. *Carbon* 2009; 47: 1701–1707. DOI: [10.1016/j.carbon.2009.02.018](https://doi.org/10.1016/j.carbon.2009.02.018).
 54. Sivamaran V, Balasubramanian V, Gopalakrishnan M, et al. Identification of appropriate catalyst system for the growth of multi-walled carbon nanotubes via catalytic chemical vapor deposition process in a single step batch technique. *Mater Res Express* 2019; 6: 105620.
 55. Lamouroux E, Serp P, and Kalck P. Catalytic routes towards single wall carbon nanotubes. *Catal Rev - Sci Eng* 2007; 49: 341–405. DOI: [10.1080/01614940701313200](https://doi.org/10.1080/01614940701313200).
 56. Sai Krishna K and Eswaramoorthy M. Novel synthesis of carbon nanorings and their characterization. *Chem Phys Lett* 2007; 433: 327–330. DOI: [10.1016/j.cplett.2006.11.068](https://doi.org/10.1016/j.cplett.2006.11.068).
 57. Liu Y, Hu W, Wang X, et al. Carbon nanorods. *Chem Phys Lett* 2000; 331: 31–34. DOI: [10.1016/S0009-2614\(00\)01143-X](https://doi.org/10.1016/S0009-2614(00)01143-X).
 58. Chen L, Wang H, Xu J, et al. Controlling Reversible Elastic Deformation of Carbon Nanotube Rings. *J Am Chem Soc*. 2011; 133: 9654–9657.
 59. Omachi H, Segawa Y, and Itami K. Synthesis and racemization process of chiral carbon nanorings: a step toward the chemical synthesis of chiral carbon nanotubes. *Org Lett* 2011; 13: 2480–2483. DOI: [10.1021/ol200730m](https://doi.org/10.1021/ol200730m).
 60. Feng C and Liew KM. A molecular mechanics analysis of the buckling behavior of carbon nanorings under tension. *Carbon* 2009; 47: 3508–3514. DOI: [10.1016/j.carbon.2009.08.021](https://doi.org/10.1016/j.carbon.2009.08.021).

61. Zhou Z, Wan D, Bai Y, et al. Ring formation from the direct floating catalytic chemical vapor deposition. *Phys E Low-dimensional Syst Nanostructures* 2006; 33: 24–27. DOI: [10.1016/j.physe.2005.10.016](https://doi.org/10.1016/j.physe.2005.10.016).
62. Ahlskog M, Seynaeve E, Vullers RJM, et al. Ring formations from catalytically synthesized carbon nanotubes. *Chem Phys Lett* 1999; 300: 202–206. DOI: [10.1016/S0009-2614\(98\)01322-0](https://doi.org/10.1016/S0009-2614(98)01322-0).
63. Wang X, Wang Z, Liu YQ, et al. Ring formation and fracture of a carbon nanotube. *Chem Phys Lett* 2001; 339: 36–40. DOI: [10.1016/S0009-2614\(01\)00291-3](https://doi.org/10.1016/S0009-2614(01)00291-3).
64. Venkatesan S, Visvalingam B, Mannathusamy G, et al. Effect of chemical vapor deposition parameters on the diameter of multi-walled carbon nanotubes. *Int Nano Lett* 2018; 8: 297–308. DOI: [10.1007/s40089-018-0252-4](https://doi.org/10.1007/s40089-018-0252-4).
65. Pol VG, Pol SV, Calderon Moreno JM, et al. High yield one-step synthesis of carbon spheres produced by dissociating individual hydrocarbons at their autogenic pressure at low temperatures. *Carbon* 2006; 44: 3285–3292. DOI: [10.1016/j.carbon.2006.06.023](https://doi.org/10.1016/j.carbon.2006.06.023).
66. Miao JY, Hwang DW, Narasimhulu KV, et al. Synthesis and properties of carbon nanospheres grown by CVD using kaolin supported transition metal catalysts. *Carbon* 2004; 42: 813–822. DOI: [10.1016/j.carbon.2004.01.053](https://doi.org/10.1016/j.carbon.2004.01.053).
67. Sivamaran V, Balasubramanian V, Gopalakrishnan M, et al. Optimizing Chemical Vapor Deposition Parameters to Attain Minimum Diameter Carbon Nano Tubes by Response Surface Methodology. *J Adv Microsc Res.* 2018; 13: 181–189. DOI: [10.1166/jamr.2018.1377](https://doi.org/10.1166/jamr.2018.1377).
68. Sivamaran V, Balasubramanian V, Gopalakrishnan M, et al. Developing empirical relationship to predict the diameter of multiwall carbon Nano tubes (MWCNTs) synthesized by chemical vapor deposition (Cvd) process. *Manufacturing Technology Today* 2017; 16: 6.
69. Sivamaran V, Balasubramanian V, Gopalakrishnan M, et al. *Gourav Rao, Mechanical and Tribological Properties Of Self-Lubricating Al 6061 Hybrid Nano Metal Matrix Composites Reinforced by NSiC and MWCNTs.* Surfaces & Interfaces Elsevier, DOI: [10.1016/j.surfin.2020.100781](https://doi.org/10.1016/j.surfin.2020.100781).
70. Kalakonda P, Kalakonda PB, and Banne S. Studies of electrical, thermal, and mechanical properties of single-walled carbon nanotube and polyaniline of nanoporous nanocomposites. *Nanomater Nanotechnology* 2021; 11: 18479804211001140. DOI: [10.1177/18479804211001140](https://doi.org/10.1177/18479804211001140).
71. Wang M, Zhang Y, Dong C, et al. Preparation and electromagnetic shielding effectiveness of cobalt ferrite nanoparticles/carbon nanotubes composites. *Nanomater Nanotechnology* 2019; 9: 1847980419837821. DOI: [10.1177/1847980419837821](https://doi.org/10.1177/1847980419837821).