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Application of Box Behnken Design to Optimize the Reaction Conditions on the Synthesis of Multi-walle d Carbon Nanotubes

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ABSTRACT

The application of the Box Behnken design methodology to arranging experiments for turning the yield of Multi-walled Carbon nanotubes (MWCNTs) synthesis by spray pyrolysis utilising Citrus *Limonum* oil as a carbon precursor and Fe/Co supported on silica as a catalyst is described in this study. The reaction temperature, catalyst composition, and precursor feed rate were chosen as the process's optimization parameters. Scanning electron microscopy, transmission electron microscopy, and Raman spectroscopy were used to characterise the as-grown CNTs. The optimal set of turning parameters for spray pyrolysis to obtain a high yield of CNTs was identified as a consequence of this research.

Keywords: Box-Behnken design; Carbon nanotube; Spray pyrolysis.

1. INTRODUCTION

Carbon nanotubes are members of the fullerene structural family that were discovered by Iijima in 1991(Iijima, 1991). These incredible structures have an enthralling mechanic, electronic and magnetic properties (Langer *et al.* 1996; Yu *et al*. 2000; Dressel Haus *et al*. 2001). The material's unique features make it suitable for use in solar cells, nanoelectronic devices, field emitters, gas storage, biosensors, and catalytic supports (Suzuki *et al*. 2003; Brattas *et al*. 2008; Yoon *et al*. 2005; Dillon *et al*. 1997; Oh *et al*. 2009 ; Pan *et al*. 2006). The most extensively utilised CNT synthesis methods include arc discharge, laser ablation, chemical vapour deposition, and spray pyrolysis (Song *et al*. 2007, Guo *et al*. 1995; Suriani *et al*. 2009; Ghosh *et al*. 2007; Kalaiselvan *et al*. 2014). Spray pyrolysis is smilar to CVD, with the exception that it is a one-step process rather than two (Kalaiselvan *et al*. 2013; 2016). Catalysts such as Fe, Co or Ni catalysts were widely used for the synthesis of single-walled and multiwalled CNTs (Kalaiselvan *et al*. 2016). The synergetic effect of the metals involved in the catalyst found to enhance the catalyst activity (Ghosh *et al*. 2008). Li *et al*. have studied the effect of temperature on the growth and structure of carbon nanotubes (Li *et al*. 2002). Natural hydrocarbons have been utilized as carbon precursor for the synthesis of CNTs such as camphor, turpentine oil, pine oil, *Cymbopogon flexuous* oil and *Helianthus annuus* oil (Afre *et al*. 2006; Kumar *et al*. 2007; Karthikeyan *et al*. 2010; Mageswari *et al*. 2014; Angulakshmi *et al*. 2013). These natural precursors are very cheap, renewable and ample of their availability. Process optimization via design of experiments has recently gained traction in a number of nanotechnology-related fields. Nourbakhsh studied the effect of process parameters on the diameter of carbon nanotubes utilizing RSM (Nourbakhsh *et al*. 2007). The science of statistically evaluating the greatest quantity of data with the fewest number of tests is known as statistical design of experiment (Goh *et al*. 2001). Using response surface methods, Liu et al. optimised the reaction conditions for the production of single-walled carbon nanotubes (Liu *et al*. 2012). As the number of factors expands, Box-Behnken designs were developed to minimise the sample size. Box-Behnken is based on a spherical, revolving design. It has been applied for the optimization of several chemical and physical processes, and the number of experiments is decided accordingly. In this study, the experiments were planned and conducted according to a Box-Behnken type response surface design. Box-Behnken experimental design is applied to investigate and optimize the reaction conditions, which affect the yield and morphology of CNTs.

2. EXPERIMENTAL METHODS

2.1 Preparation of a mixture of catalysts

The wet impregnation process was used to prepare Fe/Co catalyst supported on silica. Fe/Co catalyst supported on silica (SiO_2) particles (Fe: Co: SiO_2 =1:0.4:4) were prepared as follows. Metal salts (Merck) i.e. Fe $(NO_3)_3$. $6H_2O$ and Co $(NO_3)_2$.$6H_2O$ were dissolved in methanol and mixed thoroughly with methanol suspension of silica (Merck). The solvent was then evaporated, and the resulting cake was heated to 90-100 degrees Celsius for 3 hours before being taken from the furnace and crushed in an agate mortar. Before loading into the reactor, the fine powders were calcined for 1 hour at 450 °C and then re-ground.

2.2 Fabrication and purification of nanotubes

The synthesis of Multi-walled Carbon nanotubes (MWCNTs) was carried out using a spray pyrolysis method. The catalyst was placed on the quartz boat. The boat was placed in the heating furnace. In this experiment, the quartz tube was first flushed with nitrogen in order to remove air and create a nitrogen atmosphere and then heated to a reaction temperature. The precursor solution of *Citrus limonum* oil was sprayed into the quartz tube using nitrogen as a carrier gas. The experiments were conducted by varying the process parameters with a reaction time of 45 minutes. After cooling down to room temperature in flowing nitrogen gas, the Carbon deposit was removed from the reactor and weighed. The yield of carbon deposit was calculated according to Willems *et al.* (2000) as, Carbon deposit % = 100 $(m_{Total} - m_{Cat})/m_{Cat}$, where m_{Cat} is the initial amount of catalyst and m_{Total} is the total mass of the sample after the reaction. The as-grown products were heated with 1N HCl at 60°C for 30 min. Finally, the samples were washed with distilled water to remove the acid. The collected sample was dried at 120°C in the air for 2 hours.

A scanning electron microscope and a high–resolution transmission electron microscope were used to analyse the surface morphology of the produced carbon samples. Raman Spectroscopy was used to determine the crystalline structure of CNT samples.

2.3 Experimental Design

Box-Behnken experimental design is a three-level design based on the combination of a factorial design. For this approach, Design-Expert Software version 8, Stat-Ease, was used to design the experiment and randomize the runs. Box Behnken designs allow estimating coefficients in a second-degree polynomial regression and modelling of a quadratic response surface. In the present investigation, reaction temperature, the composition of (Fe-Co) catalyst and feed rate of precursor was considered as input variables whereas, the percentage of yield was chosen as the response variable. Table 1 shows the highest and lowest levels of independent variables. The experimental design matrix by the Box-Behnken design for the *Citrus limonum* oil is tabulated in Table 2, and the corresponding experiments were performed.

Table 1. The Experimental Range and Levels of the Input Variables for *Citrus Limonum* Oil

Input Variables	Level (-1)	Level (+1)
A:Reaction Temperature (°C)	550	750
B: Composition of Catalyst (g)	0.25	0.75
C: Feed rate of Precursor (mL)	10	30

Table 2. Box-Behnken Design Matrix and Corresponding Response for *Citrus Limonum* Oil

Run	Factor 1 A: Reaction Temp (°C)	Factor 2 B: Catalyst Composition (g)	Factor 3 C: Feed rate of Precursor (mL)	Response 1 Yield (%)
1	-1	0	-1	15
2	0	1	1	60
3	1	1	0	55
4	-1	0	1	35
5	0	0	0	78
6	0	1	-1	40
7	0	0	0	75
8	0	0	0	76
9	1	0	-1	42
10	0	0	0	72
11	0	0	0	71
12	-1	1	0	20
13	-1	-1	0	10
14	1	-1	0	50
15	0	-1	-1	37
16	0	-1	1	50
17	1	0	1	45

3. RESULTS AND DISCUSSION

3.1 Box-Behnken Design and Data Analysis

Table 3. ANOVA for RSM parameters fitted to a polynomial equation for methyl ester of *Citrus limonum* oil

	Sum of Squares	df	Mean Square	F-Value	p-value Prob > F
Model	7195.064706	9	799.4516	24.6853	< 0.0001
A-Temperature	1568	1	1568	48.4164	0.0002
B-Catalyst composition	98	1	98	3.02602	0.1255
C-Feed rate of carbon precursor	392	1	392	12.1041	0.0103
AB	6.25	1	6.25	0.19298	0.6737
AC	72.25	1	72.25	2.23092	0.1789
BC	12.25	1	12.25	0.37825	0.5580
A^2	2973.602632	1	2973.603	91.8183	< 0.0001
B^2	834.1289474	1	834.1289	25.7560	0.0014
C^2	775.9184211	1	775.9184	23.9586	0.0018
Residual	226.7	7	32.38571		
Lack of Fit	193.5	3	64.5	7.77108	0.0382
Pure Error	33.2	4	8.3		
Cor Total	7421.764706	16			

The independent process variables of reaction temperature (°C), catalyst composition (g), and precursor feed rate (mL) were explored using the Box-Behnken design methodology, and their individual and interaction impacts on the yield percentage (as a response) of MWNTs were explored. According to the Box-Behnken experimental design and input variables, the quadratic equation for predicting the optimal point was obtained, and the empirical relationship between the response and the independent variables in the coded units based on the experimental data was given by

$$Y = 74.4 + 14A + 3.5B + 7C - 1.25AB - 4.25AC + 1.75BC - 26.575A^2 - 14.075B^2 - 13.575C^2$$

ANOVA was used to determine the statistical significance of the quadratic model. Table 3 displays the results of the ANOVA for the quadratic equation. The ANOVA shows that the aforementioned quadratic equations accurately capture the actual connection between the answer and significant factors. The values of F and p determine the significance of the coefficient term; the larger the F value and the smaller the value of p, the more significant the coefficient term. The p value is less than 0.05, indicating that the model is statistically significant. The Model F value for *Citrus limonum* Oil was 24.68, indicating that there was only a 0.01 percent chance that such a large "Model F value" could occur due to noise, and that the regression equation could explain the majority of the variation in the response, and that the model was significant.. In addition, the probability $p<0.0001$ also validated that the model was significant. In the present investigation, A, C, A^2, B^2, C^2 are significant model terms for *Citrus limonum* oil. The other model terms, whose values of p were higher than 0.1000 in Table 3 were not significant.

In a system with a different number of independent variables, the adjusted R^2 (Adj-R^2) value is more suited for evaluating the model goodness of fit. In this model, the predicted R^2 0.5759 for *Citrus limonum* oil values are in reasonable agreement with the adjusted R^2 0.9302 values. The results indicated that the selected quadratic model was adequate in assuming the response variables for the experimental data. The perturbation plot can be used to find the most influential factors on the response. A steep slope or curvature in a factor shows that the response is sensitive to that variable.

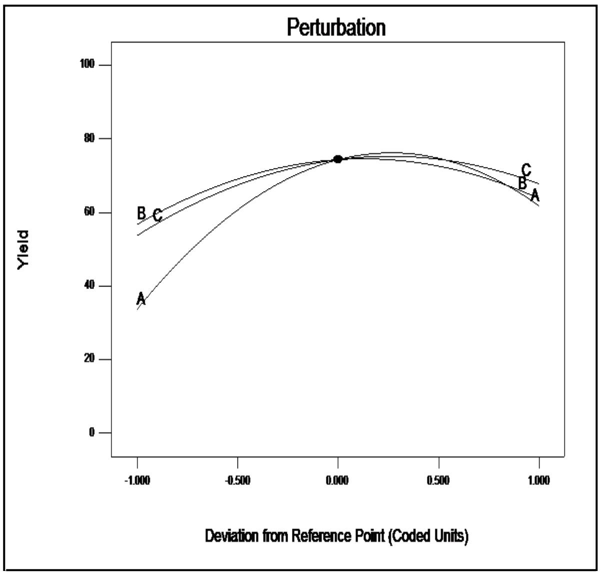

Fig. 1: Perturbation Plot for *Citrus Limonum* oil

3.1 Three Dimensional Response surface plots

Three-dimensional surfaces and two-dimensional contours were plotted to study the interaction between all three variables, with one variable held constant at the central level and the other two varying within the experimental ranges. The full range of two factors at a time can be displayed. In these 3 dimensional graphs, a steep slope or curvature in a factor shows that the response is sensitive to that factor.

In this experiment, Fig. 2 indicates that the response is sensitive to the reaction temperature. The yield percentage of MWNTs increases with an increase in temperature and attains a peak at optimum temperature (650 °C) for *Citrus limonum* oil. The low yield obtained at 550 °C and 750 °C is possibly due to the fact that the catalyst could not be activated and the high rate of pyrolysis followed by encapsulation of catalyst, respectively. The high yield obtained at 650 °C in this study is attributed to an almost equal rate of pyrolysis of precursor and CNTs growth (Kumar *et al*. 2005).

The combined effect of temperature and feed rate of carbon precursor on the yield percentage was shown in Fig. 3. As can be understood from Figure 3, increase of precursor feed rate from 10 mL to 20 mL increases the yield percentage of MWNTs. Further increase of flow rate to 30 mL leads to a reduction in the yield of MWNTs. The higher yield obtained for the precursor feed of 20 mL per hour may be attributed to the effective pyrolysis of the precursor at this experimental condition.

3.2 Numerical Optimization

Response surfaces are used to determine an optimum. Table 4 represents the solution for numerical optimization. It is possible that at this temperature, the carbon precursor was sufficiently pyrolyzed, and good interaction between the hydrocarbon and catalyst facilitated the formation of uniform carbon nanotube diameter. The optimum parameters suggested for the maximum yield of 77.11 through this experiment are reaction temperature 674.29 ° C, the Catalyst composition of 0.53g and the Feed rate of the precursor was 22.28mL. SEM and HRTEM image of as-grown CNTs under optimized condition was shown in Fig. 4 & 5. Raman spectrum of the as-grown carbon nanotube was shown in Fig. 6. Two peaks are observed at 1335 $cm^{-1,}$ and 1545cm^{-1} corresponds to the D peak and G peak. The absence of lower frequency radial breathing modes (RBM) indicated the absence of Single-walled carbon nanotubes. The I_G/I_D ratio calculated from the peak area is 1.8.

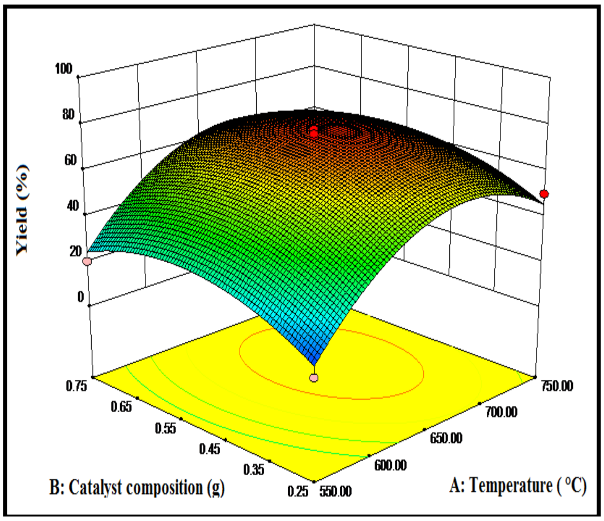

Fig. 2: The response surface plot as the function of temperature and catalyst composition

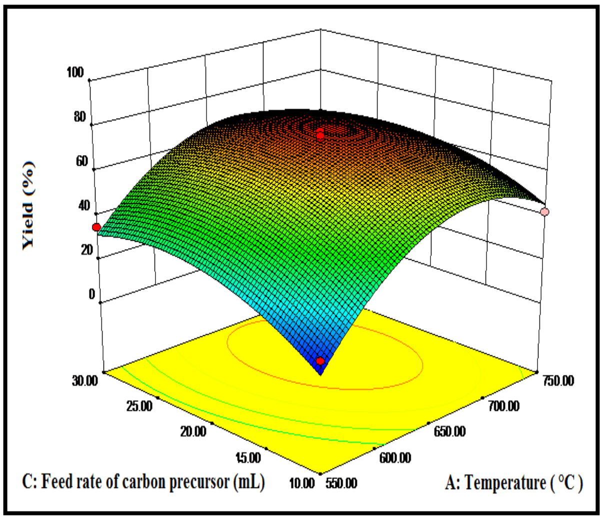

Fig. 3: The response surface plot as the function of temperature and feed rate of carbon precursor

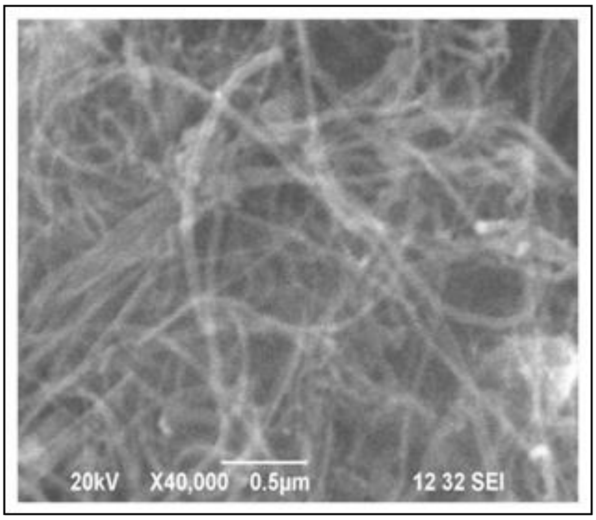

Fig. 4: SEM image of as-grown CNT at optimized condition

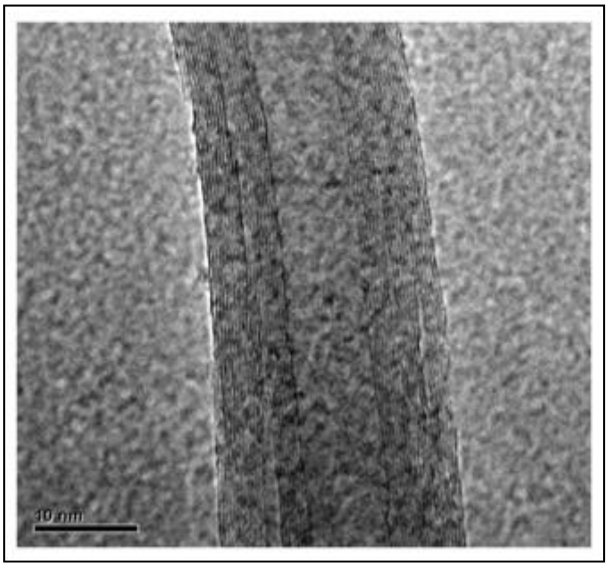

Fig. 5: HRTEM image of as-grown CNT at optimized condition

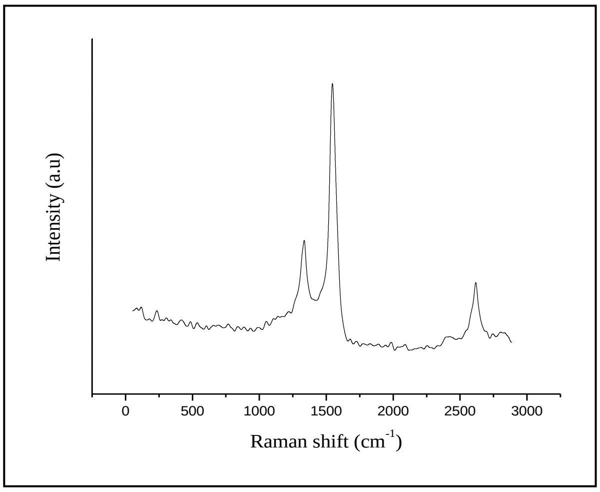

Fig. 6: Raman spectrum of as-grown CNT at optimized condition

Table 4. Obtained optimum values of the process variables and responses

Variables	**Optimum Values**
	***Citrus Limonum* oil**
Reaction temp(°C)	674.29
Catalyst composition (g)	0.53
Feed rate of Precursor (mL)	22.28
Yield percentage (Predicted)	77.11
Yield percentage (Actual)	78

4. CONCLUSION

In this study, the Response surface methodology based Box-Behnken design of the experiment was used to optimize the yield of MWCNTs synthesized using *Citrus limonum* oil as the carbon precursor. By implementing the optimal parameters, maximum yield of CNT was produced. The optimum parameters suggested through this experiment are reaction temperature 674.29 ^{o} C, the Catalyst composition of 0.53g and the Feed rate of the precursor was 22.28mL. This effective method can be applied to achieve the maximum yield of CNT in large scale industries.

REFERENCES

Angulakshmi,V. S., Rajasekar, K., Sathishkumar, C., Karthikeyan, S., Growth of vertically aligned carbon nanotubes on a silicon substrate by a spray pyrolysis method. *New Carbon Mater.*, 28(4), 284-287 (2013). https://dx.doi.org/10.1016/j.carbon.2013.07.075

Brattas, A., Nanoelectronics: Spin surprise in carbon, *Nature*, 452(7186), 419-420 (2008). https://dx.doi.org/10.1038/452419a

Dillon, A. C., Jones, K. M., Beddedhl, T. A., Kiang, C. H., Bethune, D. S. and Heben, M. J. Storage of hydrogen in single-walled carbon nanotubes, *Nature*, 386(6623), 377-379 (1997). https://dx.doi.org/10.1038/386377a0

Ghosh, P., Afre, R. A., Soga, T. and Jimbo, T., A simple method of producing single-walled carbon nanotubes from a natural precursor: Eucalyptus oil, *Mater. Lett.*, 61(17), 3768-3770 (2007). https://dx.doi.org/10.1016/j.matlet.2006.12.030

Ghosh. P., Soga, T., Rakesh, A., Afre and Jimbo, T., Simplified synthesis of single-walled carbon nanotubes from a botanical hydrocarbon: Turpentine oil, *J. Alloys Compd.*, 462(1-2), 289-293 (2008). https://dx.doi.org/10.1016/j.jallcom.2007.08.027

Goh, T. N., A Pragmatic approach to experimental design in industry, *J. Appl. Stat.*, 28 (3), 391-398 (2001). https://dx.doi.org/10.1080/02664760120034126

Guo, T., Nikolaev, P., Thess, A., Colbert, D. T. and Smalley, R. E., Catalytic growth of single-walled manotubes by laser vaporization, *Chem. Phy. Lett.*, 243(1-2), 49-54 (1995). https://dx.doi.org/10.1016/0009-2614(95)00825-O

Iijima, S., Helical microtubules of graphitic carbon, *Nature*, 354(6348), 56-58 (1991). https://dx.doi.org/10.1038/354056a0

Karthikeyan, S., Kalaiselvan, S., Manorangitham, D. and Maragathamani, D., Morphology and structural studies of multi-walled carbon nanotubes by spray pyrolysis using *Madhuca longifolia* oil, *J. Environ. Nanotechnol.*, 2(4), 15-20 (2013). https://dx.doi.org/10.13074/jent.2013.12.132040.

Kalaiselvan. S., Gopal, K. and Karthikeyan. S., Synthesis and characterization of multiwalled carbon nanotubes using *Brassica juncea* oil as carbon source, *Carbon science and technology*, 8(1), *25-31* (2016).

Kalaiselvan, S., Jothivenkatachallam, K and Karthikeyan. S., The Effect of Catalyst composition on the Growth of Multi-walled Carbon nanotubes from Methyl esters of *Oryza sativa* oil, *J. Environ. Nanotechnol.*, 5(1), 33-38 (2016). https://dx.doi.org/10.13074/jent.2016.03.161181

Kalaiselvan, S., Balachandran, K., Karthikeyan, S. and Venckatesh, R., Renewable precursor based MWCNTs synthesized by spray pyrolysis method for DSSC application, Silicon-Springer (2016). https://dx.doi.org/10.1007/s12633-016-9419-7

Karthikeyan, S. and Mahalingam, P., Studies of yield and nature of multi-walled carbon nanotubes synthesized by spray pyrolysis of pine oil at different temperatures, *Int. J. Nanotechnol. Appl.*, 4(3), 189-197 (2010).

Kumar. M., Okazaki, T., Hiramatsu, M. and Ando. Y., The use of camphor-grown carbon nanotube array as an efficient field emitter, *Carbon*, 45 (9), 1899-1904 (2007). https://dx.doi.org/10.1016/j.carbon.2007.04.023

Kumar, M. and Ando, Y., Controlling the diameter distribution of carbon nanotubes grown from camphor on a zeolite support, *Carbon*, 43(3), 533-540 (2005). https://dx.doi.org/10.1016/j.carbon.2004.10.014

Langer, L., Bayot, V., Grivei, E., Issi, J.-P., Heremans, J. P., Olk, C. H., Quantum transport in a multiwalled carbon nanotubes, *Phys. Rev. Lett.*, 76(3), 479–482 (1996). https://dx.doi.org/10.1103/PhysRevLett.76.479

Li, W. Z., Wen, J. G. and Ren, Z. F., Effect of temperature on growth and structure of carbon nanotubes by chemical vapor deposition, *Appl. Phys.* A, 74, 397-402 (2002). https://dx.doi.org/10.1007/s003390201284

Liu, W. W., Aziz, A., Chai, S. P., Mohamed, A. R. and Tye, C. T., Optimisation of reaction conditions for the synthesis of single-walled carbon nanotubes using response surface methodology, *Can. J. Chem. Eng.*, 90(2), 489-505 (2012). https://dx.doi.org/10.1002/cjce.20561

Mageswari. S., Kalaiselvan. S., Syed Shabudeen. P. S., Sivakumar. N. and Karthikeyan. S. Optimization of growth temperature of multi-walled carbon nanotubes fabricated by chemical vapour deposition and their application for arsenic removal. *Mater. Sci-Poland*, 32(4), 709-718 (2014). https://dx.doi.org/10.2478/s13536-014-0235-8

Nourbakhsh, A., Ganjipour, B., Zahedifar M. and Arzi, E., Morphology Optimization of CCVD-Synthesized multiwall carbon nanotubes, using statistical design of experiments, *Nanotechnol.*, 18(11), 01-07 (2007).

Oh, J., Yoo, S., Chang, Y. W., Lim, K. and Yoo, K. H., Carbon nanotube-based biosensor for detection hepatitis B. *Curr. Appl. Phys.*, 9(4), 229-231 (2009). https://dx.doi.org/10.1016/j.cap.2009.06.045

Pan, D., Chen, J., Tao, W., Nie, L. and Yao, S., Polyoxometalate-Modified carbon nanotubes: New catalyst support for methanol Electro-oxidation, *Langmuir*, 22(13), 5872-5876 (2006). https://dx.doi.org/10.1021/la053171w

Rakesh A. Afre, Soga. T., Jimbo, T., Mukul kumar, Ando, Y., Sharon, M., Prakash, R., Somani and Umeno, M., Carbon nanotubes by spray pyrolysis of turpentine oil at different temperatures and their studies, *Microporous Mesoporous Mater.*, 96(1-3), 184-190 (2006). https://dx.doi.org/10.1016/j.micromeso.2006.06.03

Song, X., Liu, Y. and Zhu, J., Multi-walled carbon nanotubes produced by hydrogen DC arc discharge at elevated environment temperature, *Mater. Lett.*, 61(2), 389-391 (2007). https://dx.doi.org/10.1016/j.matlet.2006.04.068

Suzuki, K., Yamaguchi, M., Kumagai, M. and Yanagida. S., Application of carbon nanotubes to counter electrodes of dye-sensitized solar cells, *Chem. Lett*., 32(1), 28-29 (2003). https://dx.doi.org/10.1016/j.elecom.2006.10.028

Suriani, A. B., Azira, A. A., Nik, S. F., Md Nor and Rusop, M., Synthesis of vertically aligned carbon nanotubes using natural palm oil as carbon precursor, *Mater. Lett.*, 63, 2704-2706 (2009).

Yoon, B. J., Hong, E. H., Jee, S. E, Yoon, D. M., Shim, D. S., Son, G. Y., Lee, Y. J., Lee, K. H., Kim, H. S. and Park, C. G., Fabrication of flexible carbon nanotube field emitter arrays by direct microwave irradiation on organic polymer substrate, *J. Am. Chem. Soc.*, 127(23), 8234-8235 (2005). https://dx.doi.org/10.1021/ja043823n

Yu, M. F., Files, B. S., Arepalli, S. and Ruoff, R. S., Tensile loading of ropes of single wall carbon nanotubes and their mechanical properties, *Phys. Rev. Lett.*, 84(24), 5552–5555 (2000). https://dx.doi.org/10.1103/PhysRevLett.84.5552