Optimization of Experimental Conditions for Fabrication of Carbon Nanotubes Based on Taguchi Robust Design Method

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(Received: 27 May 2009 and accepted: 25 Oct. 2009)

Abstract:
Carbon nanotube, a new structure of carbon element, is composed of graphene sheets rolled into closed concentric cylinders with diameter of the order of nanometers and length of micrometers. Liquid arc discharge was used for fabrication of carbon nanotubes, and subsequently a modified acid treatment method applied for purification stage. A statistical design of experimental (DOE) (Taguchi method with L16 orthogonal array robust (OA) design and Qualitek-4 software) was implemented in this work to optimize the process. Voltage, current, catalyst type and plasma were considered as process parameters to be optimized. As the result of taguchi analysis in this study, voltage and catalyst were the most influencing parameters on the yield production of carbon nanotubes (~4.121 mg min^{-1} purred CNTs). The maximum product yield of CNTs were obtained at voltage of 25, LiCl (o.25 M) as a salt in solution, Ni/Mo as a co-catalyst and the catalyst ratio of. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were utilized to study the morphology of these carbon nanotubes.

Keywords: *liquid arc discharge, Taguchi method, Design of experiment, Carbon nanotube, synthesis, optimization*

1- INTRODUCTION

Carbon nanotubes have many potential applications including material as a good conductor, quantum wires, nano-devices and field-effect transistors, storage of gas and AFM tip. These wide applications of CNTs are due to their unique structural and excellent physical and electronic properties. liquid Arc-discharge method is developed to synthesize many kinds of nano-carbon structures such as carbon onions, carbon nanohorns and carbon nanotubes. This technique is considered as a low cost method since it does not require any expensive equipment.

The number of publications on carbon nanotubes (CNTs) and CNT-reinforced composite materials has rapidly grown since CNTs were discovered by Iijima (1991) more than a decade ago, as evidenced by several recent review articles on mechanical behavior, fabrication and applications of such materials (Xu et al., 2004).

Three typical synthesis methods have been developed for the production of CNTs, including the conventional arc discharge in an inert gas atmosphere (argon, helium) (or hydrogen), laser vaporization and chemical vapor deposition (CVD) (Zhu et al., 2002). Traditional arc discharge requires a complicated vacuum and heat exchange system. Laser vaporization produces high quality CNTs but demands considerable power. The yields of the above two methods are very low (~mg/h) (Wang et al., 2005). On the other hand, it is also hard to produce high-quality CNTs through CVD technique yet (Zhu et al., 2002). Arc discharge in liquid environments is a new developed method to synthesize the CNTs. In this method, a DC power supply and an open vessel full of liquid nitrogen, deionized water or aqueous solution is required. This method does not require any vacuum equipment, reacted gases, high temperature furnace or heat exchangeing system. Indeed, the liquid substituted both vacuum and cooling system (Lang et al., 2005). Consequently, this method is extremely simple and cheap (Wang et al., 2005). Until now, different types of carbon nanostructured have been successfully synthesized by this method (Zhu et al., 2002). Properties of carbon nanotube obtained by this method are affected by various parameters such as the voltage, current, types of the catalyst, nature of solution and so on. The interrelationships between the above parameters are complex, and the analysis of optimization of the factors is a time consuming work.

The full factorial design is referred as the technique of defining and investigating all possible conditions in an experiment involving multiple factors while the fractional factorial design considers only a fraction of all possible combinations. Although these approaches are widely used, they have certain limitations: they are inefficient in time and cost when the number of the variables is large; they require hard mathematical treatment in the design of the experiment and in the analysis of the results; the same experiments may have different designs thus produce different results; further more, determination of contribution of each factor is normally not permitted in this kind of design. The Taguchi method has been proposed to overcome these limitations by simplifying and standardizing the fractional factorial design (Atil et al., 2005). The methodology involves identification of controllable and uncontrollable parameters and the establishment of a series of experiments to find out the optimum combination of the parameters which has the greatest influence on the performance and the least variation from the target of the design. (Roy, 2003)

The efficient analysis of a complex system using the Taguchi method has been performed recently (Ting et al., 2006 and Yang et al., in press). The taguchi method follows these steps: (1) determination of controllable factors and their levels; (2) identification of uncontrollable factors and test conditions; (3) design of Taguchi crossed array layout; (4) execution of experiments according to trial conditions; (5) analysis of results; (6) determination of optimal run; (7) confirmation of optimum run.

In this study, fabrication of CNTs by arc-discharge technique in solution and its purification with the modified acid treatment method, which has lowest side effect on the CNTs, is investigated. Furthermore, the Taguchi design method is applied for optimization of the process to obtain up to standard carbon nanotube in different ways by using optimal synthesis conditions.

2. MATERIAL & SET UP

2.1. Materials

All chemicals of analytical grade and aqueous solutions were prepared with doubly distilled water. The arc discharge apparatus employed in this study was comprised of an open vessel, graphite electrodes, and a DC power supply. The diameters of anode and cathode were 6 mm and 12 mm, respectively. The anode was drilled a 2 mm diameter hole and filled with catalysts powder in each experiment.

2.2. Fabrication and purification method

The brass electrode holders were free to move forward and backward, which permitted proper electrode gap adjustment to be made during arc discharge (Figure 1). It should be noted that, the discharge in liquid environments is erratic, thus it is critical to control precisely the arc gap in order to run the arc stably.

Upon ignition, to avoid arc disruption, the electrode gap was maintained at 1 mm. A digital controllable power supply was used. The arc lasted for 120 seconds. The discharge current for all experiments was sustained at 100A at which the arc showed to be quite stable and the voltage was adjusted for each. Evaporation of the solution during the arc discharge was considered to be negligible. Different metallic catalysts with various ratio were applied which are going to explain. Taguchi's orthogonal array table was used to optimum the weight of the pure carbon nanotubes by choosing four parameters that could affect the synthesis of carbon nanotube. Table 1 show the parameters and levels were used in this experiment.

The as-prepared deposit was purified using different combinations of the following purification steps for all tests: first, sonicating 0.5 g of as-prepared deposit in 12 NHCl for 30 minutes and leaving the resulting solution to stand overnight. Then it was refluxed in 6 N HCl for 6 hours. After treating the deposit with acid, the resulting solution was diluted with distilled water and centrifuged. After centrifugation, the supernatant solution was decanted and the residue was transferred on to a Millipoor filter paper. The residue on the filter paper was washed with distilled water (4–5 times) to remove the acid. The residue was dried in an oven at 80–100ºC for 5 hours. Then the carbon nanotubes were weighted and kept in desiccators (Mathur et al., 2007; Feng et al., 2003).

2.3. Taguchi methodology

2.3.1. Software

Qualitek-4 software (Nutek Inc., MI) for automatic design of experiments using Taguchi approach was used at the present study. Qualitek-4 software is equipped to use L-4 to L-64 arrays along with selection of 2 to 63 factors with two, three and four levels to each factor. The automatic design option allows Qualitek-4 to select the array used and assign factors to the appropriate columns.

2.3.2. Design-of-experiments (DOE)

Ishigami et al. reported the first production of MWCNTs by arc discharging in liquid nitrogen (2000) but the strong evaporation resulting from the operation of the arc discharge does not allow a good thermal exchange between the synthesized material and its surroundings. Therefore, liquid nitrogen provides less efficient cooling in comparison to deionized water, and the CNTs produced in this way exhibit a distorted morphology and a degraded structure (Wang et al., 2005). Arc discharge in deionized water and liquid nitrogen are erratic due to their electrical insulation (Lang et al., 2003). The electrical conductivity of NaCl and alkaline salt solution is better than deionized water and liquid nitrogen (David, 2005). In this study Dionized water, NaCl, KCl and LiCl were used as aqueous solution .The range used for voltage was 20 to 35 volt. A metal catalyst is necessary for growth of the SWCNTs in all methods used for synthesis of CNT. Catalysts usually used to prepare SWCNTs include transition metals in single or binary mixture of metals as Fe, Co, Ni or Mo. Table 1 shows the four key parameters in the four experimental levels that affect the synthesis of carbon nanotube.

2.3.3. Design of Taguchi crossed array layout

The Taguchi crossed array layout consists of an inner array and an outer array. The inner array is made up of the orthogonal array (OA) selected from all possible combinations of the controllable factors. The outer array contains combinations of the uncontrollable factors. It can be seen from Table 1 that there are four factors, each in four levels. Table 2 shows the complete DOE experimental results used in the process of optimization study and the result. Only 16 experiments were designed, which were sufficient for our case. For each of the four parameters and for each experiment, the experimental levels (1–4) are shown in Table 2. Each level corresponds to a value, as shown in Table 1.

2.3.4. Signal-to-noise ratio

Noise factors are known as uncontrollable factors. The ideal product will only respond to the operator's signals and will be unaffected by random noise factors (weather, temperature, humidity, etc.). Therefore, the goal of quality improvement effort can be stated as an attempt to maximize the signal-to-noise ratio for the respective product. Taguchi is developed a formulation in which the ratio of controllable factors (signal factors) to uncontrollable factors (noise factors) S/N based on variance is

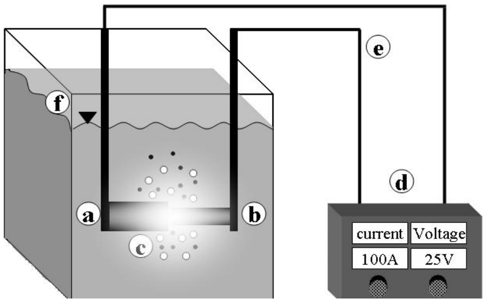

Figure 1: The schematic setup arrangement, a) cathode graphite b) Anode graphite c) Arc Plasma d) DC Arc Supplier e) wires f) Water surface.

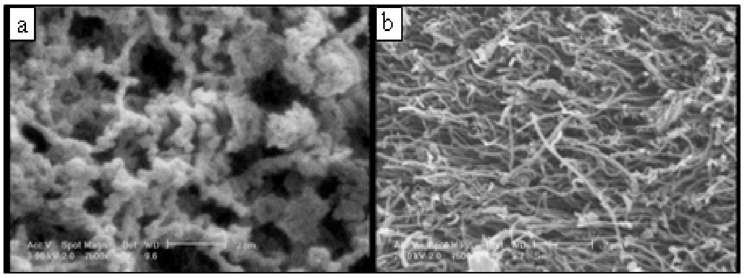

Figure 2: The SEM images of produced CNTs a) before b) after purification stage

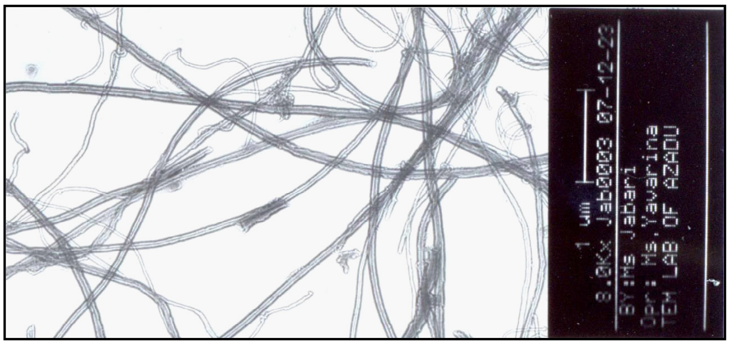

Figure 3: TEM micrograph of the carbon nanotubes after purification step.

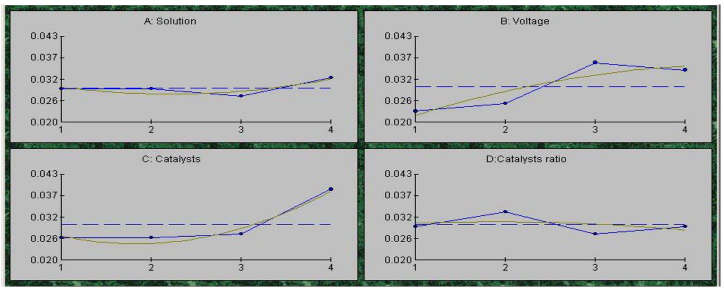

Figure 4: Response graph for significant factors. The horizontal axis shows the different levels of the each significant factor. The lines represent the trend of each factor with respect to different levels.

Table 1: Parameters and levels used in these experiments

Parameters	**Levels**			
Levels No.	1	2	3	4
A: Solution	Dionized water	NaCl (0.25M)	KCl (0.25M)	LiCl (0.25M)
B: Voltage	35	30	25	20
C: Catalyst	Ni/Ni	Ni/Fe	Ni/Co	Ni/Mo
D: Catalyst ratio	1/1	1/2	1/3	1/4

Table 2: Experimental values for carbon nanotube weight and S/N ratio after purification (Taguchi orthogonal array table of L-16)

Exp. No.	**Experimental conditions**				**Net weight (mg/min)**		**S/N ratio (dB)**
	A	**B**	**C**	**D**	**Run 1**	**Run 2**	
1	1	1	1	1	0.6	1.4	3.861
2	1	2	2	2	1.2	1.55	8.535
3	1	3	3	3	2.05	2.3	12.726
4	1	4	4	4	2.75	2.55	14.466
5	2	1	2	3	0.95	1.25	6.605
6	2	2	1	4	1.6	1.5	7.989
7	2	3	4	1	2.65	2.75	14.643
8	2	4	3	2	2.1	1.85	11.879
9	3	1	3	4	0.75	1.15	4.992
10	3	2	4	3	1.85	1.6	10.687
11	3	3	1	2	2.3	2.05	12.726
12	3	4	2	1	2.1	1.95	12.131
13	4	1	4	2	2.8	2.55	14.538
14	4	2	3	1	1.45	1.75	9.988
15	4	3	2	4	1.8	2.05	11.654
16	4	4	1	3	1.9	1.55	10.622

independent of target value and is consistent with Taguchi´s quality objective. From the quality point of view, there are three possible categories of the quality characteristics. They are: (1) smaller is better; (2) nominal is better; (3) bigger is better (Atil et al., 2000).

These are:

Smaller-the-better: in cases where minimization the occurrences of some undesirable product characteristics are desired, *S/N* ratio would be calculated by Eq. (1):

$$S/N(s) = \text{-10 } \log_{10}[\frac{1}{n}\sum Y_i^2] \quad (1)$$

Where, *S/N*(*s*) is the resultant *S/N* ratio; *n* is the number of observation on the particular product, and *Y* is the respective characteristics.

Nominal-the-best: here, by using a fixed signal value (nominal value) and the variance around this value can be considered as the result of noise factors, *S/N* ratio can be computed by Eq. (2):

$$S/N(N) = \text{-10 } \log_{10}[Mean/Variance] \quad (2)$$

Larger-the-better: The Taguchi method uses the signal-to noise ratio to express the scatter around a target value. A high value of *S/N* implies that the signal is much higher than the random effects of the noise factors. The noise is usually due to the uncontrollable factors, which exist in the environment, often cannot be eliminated and cause variations in the output.

In this study the main goal of design was maximization of net weight of pure CNT synthesized so the larger-the-better method is utilized, which would compute by Eq. (3):

$$S/N = \text{-10 } \log_{10}[\frac{1}{n}\sum(\frac{1}{Y_i})^2] \quad (3)$$

Where *Y* is the net weight of pure CNT (mg) and *n* in this study equals to 4. *S/N* ratio results are shown in Table 2.

3. RESULTS AND DISCUSSION

3.1. Analysis of the carbon nanotube purification

Figure 2 illustrates the SEM images of carbon nanotube before and after purification. Figure (2b) shows the SEM image of purified carbon nanotubes in which some impurities have been removed by the describe method. By all appearances it is cleaner than that in Figure (2a), which is the SEM image of as-grown CNTs. Comparing two images it can be concluded that the carbon and catalyst impurities are almost completely removed in this process. Figure 3 shows a TEM micrograph of the carbon nanotubes after purification step. It has been observed that the CNTs ara in hight quality, have narrow distribution diameters and quite clean surface.

3.2. Analysis of variance

The knowledge of the contribution of individual factors is critically important for the control of the final response. The analysis of variance (ANOVA) is a common statistical technique to determine the percent contribution of each factor in experimental results. It calculates parameters which known as sum of squares (SSs), pure SS, degree of freedom (DOF), variance, F-ratio and percentage of each factor. Since the procedure of ANOVA is very complicated and employs a considerable statistical formulas, only a brief description is given as follow:

The SS is a measurement of the deviation of the experimental data from the mean value of the data. The total deviation equals SS of all results minus correction factor (CF), which could be calculated from eqs. (4) and (5), respectively.

$$SS = \sum_{i=1}^{16} SN_i^{\,2} - CF \quad (4)$$

$$CF = \frac{(\sum_{i=1}^{16} SN_i)^2}{N} \quad (5)$$

DOF measures the amount of information that can be uniquely determined from a given set of data. The variance describes the distribution of the data about the mean of the data. Since the data is representative

Table 3: The ANOVA table of net weight of carbon nanotube synthesized.

Factors	DOF	SS	Variance	F-Ratio
A:Solution	3	1.155	0.375	0.975
B:Voltage	3	15.080	5.026	12.724*
C:Catalyst	3	15.693	5.231	13.241*
D:Catalyst ratio	3	2.375	0.791	2.004
Error	19	7.505		
Total	31			

* Main significant parameter

Table 4: Yield of produced CNTs after purification and consumption rate of anode electrode at the optimum condition.

	No.			
	1	**2**	**3**	**4**
product yield of CNTs (mg/min)	2.984	4.121	3.445	3.110
consumption rate of anode electrode (mg/min)	1.620	3.282	2.583	2.118

of only a part of all possible data. DOF is used in the variance calculation without considering the number of observed data. F-ratio is the ratio of variance due to the effect of a factor and variance due to the error term. It is used to measure the significance of the factor under investigation with respect to the variance of all the factors included in the error term. Pure SS is the SS minus the DOF times the error variance.

The percent contribution of each factor is the ratio of the factor sum to the total expressed in percent. When the variance of the error is zero, the F-ratio for factors A, B, C and D is undetermined. Then the variance of the error can be combined with another smallest factor variance (factor A in the current study) to calculate a new error variance which can be used to produce meaningful results. The process of disregarding an individual factor's contribution and then subsequently adjusting the contribution of the other factor is known as pooling.

After all the above-mentioned steps, the calculated parameters are organized in a standard tabular format, known as ANOVA table (Table 3). The purpose of the analysis of variance (ANOVA) is to determine their ratios percentage of affecting parameters on the CNT synthesis. The results of ANOVA analysis of raw data for maximum yield of CNT are shown in Table 3. The $F_{(0.05,2,17)}$ was 19.437 for a level of significance equal to 0.05 (or 95% confidence level). From Table 3, it is apparent that the F-values of factor B and factor C were all greater than $F_{(0.05,3,19)}$=8.6602 and the Factor A and D were not a significant influencing parameter for maximum yield of CNT. F-values of A and $D_{(2.004,\ 0.975)}$ were less than $F_{(0.05,3,19)}=8.6602$. Therefore voltage and catalyst have the most significant effect on CNT synthesis.

3.3. Determination of optimum runs

Table 3 and Figure 4 show the main results. It can be recognized that the voltage and type of catalyst have the most effects on the carbon nanotube synthesis. The optimum conditions can be determined through the response table of the ANOVA. Therefore, based on the S/N and ANOVA analysis, the optimal parameters for carbon nanotube production are the solution LiCl (level 4), 25 V as voltage (level 3), Ni/Mo as catalyst (level 4) and the catalyst ratio must be ½ (level 2). The estimated result by taguchi method was ~4.121 mg min^{-1} and the pure carbon nanotubes were achieved in optimum conditions.

3.4. Confirmation of optimum runs

The optimum run may not be necessarily among the many experiments that were already carried out, since OA represents only a small fraction of all the possibilities. It is recommended to run a confirmation experiment once the optimum condition is determined. Table 4 shows the results which were obtained by performing the experiment at the optimum test condition by repeating the four times. Table 4 reveals a good agreement between the experimental results and estimated results of Taguchi method. Also it shows product yield of CNTs (mg/min) and consumption rate of anode electrode (mg/min). It shows that the consumption rate of the anode increases with any increase in the yield weight value.

4. CONCLUSION

Fabrication of carbon nanotubes using arc discharge method in liquid solution have been carried out successfully. In order to remove the impurities from samples a modified acid treatment was applied. The whole impurities were removed after purification. It also has been shown that yield of carbon nanotube can be maximized by careful control of production parameters such as kind of plasma, voltage as well as ratio of catalysts. In addition, Taguchi design method with four parameters and in four levels which determined 16 experiments were used to optimize the parameter values for obtaining desired products. As the result of Taguchi analysis in this study, the voltage, and catalyst were the most influencing parameters on the product yield of carbon Nanotubes. The maximum product yield of CNTs were obtained at 25 voltage, LiCl as a salt in solution, Ni/Mo as a co-catalyst and the catalyst ratio of (4.121 mg min^{-1}). It has been found that a high yield of carbon nanotubes will cause a high erosion of anode electrode and vise versa. Application of a full automatic arc discharge set up and entire characterization of the produced carbon nanotubes will be the subject of our future publication.

ACKNOWLEDGMENTS

The Authors would like to thank the support of Nanobiotechnology Research Laboratory of Babol University of technology, Iran. Also special thanks of Electroanalytical Chemistry Research Laboratory of Mazandaran University.

Nomenclature

ANOVA	analysis of variance
CF	correction factor
CNT	Carbon nanotube
CVD	chemical vapor deposition
DC	direct current
DOE	Design of experimental
DOF	Degree of freedom
MWCNT	multi wall carbon nanotube
OA	orthogonal array
SS	sum of square
SWCNT	single wall carbon nanotube

References

1. Atil, H. and Y. Unver; "A Different of Experimental Design: Taguchi Method," Biological Sciences, 3, 1538-1540 (2000).
2. David, R. Lide; CRC Handbook of Chemistry and Physics, 85th ed., p.938, New York, U.A.S. (2005).
3. Feng, Y., G. Zhou, G. Wang, M. Qu and Z. Yu; "Removal of some impurities from carbon nanotubes," Chemical Physics Letters, 375 645–648 (2003).
4. Iijima, S.; "Helical Microtubules of graphitic Carbon," Nature, 354, 56–8 (1991).
5. Ishigami M., J. Cumings, A. Zettl and S. Chen; "A simple method for the continuous production of carbon nanotubes," Chemical Physics Letters, 319, 457–459 (2000).
6. Lange, H., M. Sioda, A. Huczko, Y. Q. Zhu, H. W. Kroto and D. R. Walton; "Nanocarbon production by arc discharge in water," Carbon, 41, 1617–1623 (2003).
7. Mathur, R. B., S. Seth, Ch. Lal, R. Rao, B. P. Singh, T. L. Dhami and A. M. Rao; "Co-synthesis, purification and characterization of single- and multi-walled carbon nanotubes using the electric arc method," carbon, 45, 132-140 (2007).
8. Roy, R.; Design of Experiments Using the Taguchi Approach: 16 Steps to Product and Process Improvement, John Wiley, New York, U.S.A (2001).
9. Sano, N., H. Wang, M. Chhowalla, I. Alexandrou, G. A. J. Amaratunga, M. Naito and T. Kanki; "Fabrication of inorganic molybdenum disulfide fullerenes by arc in water," Chemical Physics Letters, 368, 331–337 (2002).
10. Ting, J., Ch. Chang, Sh. Chen, D. Lu, Ch. Kung and F. Huang; "Optimization of field emission properties of carbon nanotubes by Taguchi method," Thin Solid Films, 496, 299–305 (2006).
11. Wang, Sh., M. Chang, K. M. Lan, Ch. Wu, J. Cheng, H. Chang; "Synthesis of carbon nanotubes by arc discharge in sodium chloride solution," Carbon, 43, 1792–1795 (2005).
12. Xu, Z., X. Chen, X. Qu, J. Jia and Sh. Dong; "Single-wall carbon nanotube-based voltammetric sensor and biosensor," Biosensors and Bioelectronics, 20, 579–584 (2004).
13. Yang K., E. Teo, and F. K. Fuss; "Application of Taguchi method in optimization of cervical ring" cage J. Biomech. In press.
14. Zhu, H. W., X. S. Li, B. Jiang, C. L. Xu, Y. F. Zhu, D. H. Wu and X. H. Chen; "Formation of carbon nanotubes in water by the electric-arc technique," Chemical Physics Letters, 366, 664–669 (2002).