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Yield optimization of nanocarbons prepared via chemical vapor decomposition of carbon dioxide using response surface methodology

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ABSTRACT

In this study, the effect of temperature, carbon source flow rate, and catalyst loading on the yield and morphology of the carbon nanotubes obtained via the direct decomposition of CO_2 in the chemical vapor decomposition (CVD) method has been investigated. An experimental design based on response surface methodology (RSM) was employed to investigate and optimize the effect of the reaction parameters on the yield of the obtained nanocarbons, and the most significant factor was found to be the reaction temperature. The carbon deposition amount was measured using the energy-dispersive X-ray spectroscopy (EDS) results. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) micrographs were used to illustrate the structure and morphology of the obtained nanocarbons. The crystallography of the obtained nanocarbons at various temperatures was characterized by the X-ray diffraction (XRD) patterns. Raman spectrum of the obtained CNTs showed that the ratio of the intensity of the G band to D band (I_G/I_D) for the CNTs obtained at 1100 °C is equal to 0.8 which is indicative of a crystalline structure with few defects. Moreover, the formation of multi-walled carbon nanotubes (MWCNTs) was confirmed using thermogravimetric analysis (TGA).

1. Introduction

In recent years, carbon nanotubes (CNTs) have gained much attention for their unique electrical, optical, thermal, and mechanical properties [1]. The potential of CNTs in electronics is due to their super high current-carrying capacity, ballistic electron transport, and excellent field-emission properties. Numerous CNT-based devices, such as field-effect transistors, nonvolatile random access memories, sensors, field-emission displays, and organic solar cells, have been developed and reported in the literature [2]. However, mass production of both single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) with fewer impurities is still a challenge [3]. A number of methods have been employed to produce carbon nanotubes such as plasma enhanced chemical vapor deposition (PECVD), catalytic chemical vapor deposition (CCVD), laser ablation, arc discharge, and high pressure CO conversion (HipCO) [4]. The CVD processes are important in numerous industrial applications [5]. CCVD, of all the mentioned synthesis methods, is one of the most promising means to grow carbon nanotubes [6]. In this approach, CNTs are synthesized using a carbon containing source (usually in gaseous form) at elevated temperatures in the presence of a transition metal catalyst [7]. The CCVD method has a number of advantages which make it stand out when compared with other available synthesis methods. Firstly, the product tends to contain fewer impurities in the form of graphite or metal nanoparticles. Secondly, the growth occurs at lower temperatures (550–1000 °C) [8], making the process more efficient from an economical standpoint. Lastly, the metal catalyst can be supported by a substrate, which results in the growth of aligned nanotubes in a desired direction with respect to the substrate [9]. However, controlling the reaction parameters in this method, including temperature, carbon source flow rate, and catalyst loading, plays a crucial role in the CNT production as they will affect the diameter and morphology of the obtained nanocarbons as well as the deposition yield [10].

Response surface methodology (RSM) is an empirical statistical approach in which quantitative data is obtained from appropriately designed experiments in order to identify the best regression model and operating conditions [11,12]. This technique employs a factorial design in order to construct mathematical models which describe the effects of several factors on the response. This statistical approach is a suitable technique for multi-factor experiments and has the advantage of identifying the most favorable conditions of the process by determining the common relationship between various factors. In this paper, the RSM method was employed as a useful method to investigate the effect of temperature, carbon source flow rate, and catalyst loading on the yield of the obtained nanocarbons.

Transition metals are the most common catalysts used for the synthesis of CNTs [13]. In addition, a number of transition metals, which do not exhibit catalytic activity in the form of pure metals, show catalytic activity when used in the form of oxides [14]. On the other hand,

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Table 1
Factors and levels used in this experimental design (DOE).

Factor	Low level (−1)	High level (+1)
Temperature (C) (X_1)	700	1100
Catalyst (g) (X_2)	8	10
Flow rate ($cm^3\ min^{-1}$) (X_3)	600	900

CNTs have been grown using semiconductors such as silicon (Si) and germanium (Ge) nanoparticles as substitutions for catalysts despite the fact that carbon has little solubility in bulk Si or Ge. For this purpose, these nanoparticles are required to be heated in air just before the CVD process [15–17]. It is also important to note that the yield and the quality of the obtained CNTs are greatly affected by the catalyst-support interaction as well as the support material and its textural properties. Commonly used supports in the CVD process include graphite, quartz, silicon, silicon carbide, silica, alumina, alumino-silicate (zeolite), CaCO, and magnesium oxide [18]. Among the mentioned substrates, MgO has the advantage of easy removal by dissolving in acids after the CNTs production [19]. Therefore, in this study, Ge nanoparticles were used in combination with MgO support for the production of CNTs in the CVD process.

The carbon precursor also plays an important role in the production of carbon nanotubes. By the selection of a right precursor with a right vapor pressure, both the catalyst's lifetime and the CNTs' growth rate can be increased. Subsequently, the quality and the yield of the obtained carbon nanotubes can be enhanced [18]. One of the most important factors for selecting a precursor is its molecular structure [20]. It has been reported that linear hydrocarbons such as methane, ethylene, and acetylene decompose into linear dimers/trimers of carbon by heat, and, therefore, produce straight hollow CNTs. On the other hand, cyclic hydrocarbons such as benzene, xylene, cyclohexane, and fullerene produce relatively curved/hunched CNTs with the tubes' walls often bridged from the inside [21]. Recent studies have also reported the use of carbon dioxide (CO_2) as a unique source of carbon for the production of CNTs in the CVD process [22,23]. Compared to the most widely used carbon precursors, CO_2 is competitively less expensive with a relatively high carbon yield [24]. In addition to the mentioned application of CO_2, the use of CO_2 laser flash evaporation in a CVD process is a novel approach for delivery of solid precursors with low volatility [25]. In this paper, nanocarbons have been prepared using the CVD method through CO_2 decomposition in the presence of MgO supported Ge nanoparticles. Temperature and thermal layer boundaries are among important factors in CVD processes [26]. Therefore, in this study, the effect of temperature, CO_2 flow rate, and catalyst loading on the morphology of the obtained nanocarbons has also been investigated. To our knowledge, this study is the first to investigate the effect of synthesis factors on the yield of the nanocarbons prepared via direct decomposition of CO_2 in the presence of carbon-family metallic nanoparticles.

Table 2
RSM design matrix and the experimental responses for the study of the effect of reaction parameters. The three independent variables were denoted as x_1, x_2, and x_3 which represent temperature, catalyst loading, and gas flow rate, respectively.

Runs	X_3 (flow (ml/min))	X_2 (catalyst (g))	X_1 (temperature (°c))	Carbon deposit (g)
1	900	10	1100	41
2	800	9	900	21
3	700	10	1100	39
4	800	9	900	20
5	700	10	700	13
6	800	9	900	21
7	900	8	700	15
8	900	10	700	16
9	700	8	1100	37
10	900	8	1100	40
11	700	8	700	12
12	800	9	900	22
13	800	9	900	22.5
14	963.3	9	900	24
15	800	7.367	900	20
16	636.7	9	900	17
17	800	9	900	19
18	800	10.633	900	24
19	800	9	1226.6	40
20	800	9	573.4	11

Table 3
Analysis of variance for the carbon deposit (CD) response obtained under various synthesis conditions.

Source	*Df*[a]	F-value[a]	Probability
Model	10	25.02	<0.0001
Blocks	1	4.29	0.068
Linear	3	77.13	<0.0001
Flow	1	5.14	0.05
Catalyst	1	1.36	0.274
Temperature	1	224.9	<0.0001
Square	3	4.83	0.029
Flow * flow	1	0.9	0.368
Catalyst * catalyst	1	2.9	0.123
Temperature * temperature	1	11.99	0.007
2-Way interaction	3	0.02	0.997
Flow * catalyst	1	0.02	0.899
Flow * temperature	1	0.02	0.899
Catalyst * temperature	1	0.02	0.899

[a] df, degrees of freedom; F, variance ratio.

2. RSM

Central composite design (CCD), which is a popular response surface method for the experimental design, was employed to optimize the amount of carbon deposit (CD) [27]. The objective of employing CCD was to optimize the effects of the variables to get the best response. This design has the following components: 1- a full or fractional factorial points, 2- an additional design (a star design) at a distance of α ($\alpha = 2^{(k-p)/4}$) calculated from the center, and 3- a central point. The total number of experiments can be calculated by $N = k^2 + 2k + c_p$ in which k is the factor number and c_p is the number of replications of the experiment at the central point [28]. For statistical calculations, the actual variables can be converted to coded variables using the relation below:

$$X_i = \frac{x_i - x_0}{\partial x} \quad (1)$$

where X_i is a coded value of the variable, x_i is the actual value of the variable, x_0 is the actual value of X_i at the center point, and ∂x is the step change of the variable. In this design of experiment (DOE) the design was composed of three factors (temperature, catalyst loading, and gas flow rate) with two levels (low, high), and a total of 20 runs were carried out to optimize the chosen variables. For the purpose of statistical computations, the three independent variables were denoted as x_1, x_2, and x_3, respectively. The range of the values used for the levels of each factor investigated in the experiments is selected based on the preliminary experiments and are listed in Table 1. The quadratic equation can be used for this methodology to fit the response variables:

$$Y = \beta_0 + \sum_{i=1}^{k} k\beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x_i^2 + \sum_{i}^{i<j} \sum_{j} \beta_{ij} x_i x_j \quad (2)$$

where Y, k, β_0, β_i, β_{ii}, and β_{ij} are the predicted response variable, number of variables, a constant term, coefficients of the linear parameters, coefficients of the quadratic parameters, and coefficients of the interaction parameters, respectively. The coefficient of determination (R^2) can be estimated to test the certainty of the above polynomial model [29].