Prediction of the Carbon nanotube quality using adaptive neuro–fuzzy inference system

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Abstract

Multi-walled carbon nanotubes (CNTs) are synthesized with the assistance of water vapor in a horizontal reactor using methane over Co-Mo/MgO catalyst through chemical vapor deposition method. The application of Adaptive Neuro-Fuzzy Inference System (ANFIS) technique for modeling the effect of important parameters (i.e. temperature, reaction time and amount of H2O vapor) on the quality of the CNT process is investigated. Using experimental data, qualities of CNTs are determined for training, testing and validation of developed ANFIS model. From the analysis carried out by the ANFIS-based model, the mean square deviation and a regression coefficient are found to be 4.4% and 99%, respectively. The validation results confirm that the ability of the proposed ANFIS model for predicting the quality of the CNT process over a wide range of operational conditions. In addition, sensitivity analysis indicates that the temperature has the significant effect (i.e. 94%) on the quality of the CNT process.

Keywords: ANFIS Modeling; Carbon nanotube; Co-Mo/MgO catalyst; Nanomaterials; Raman spectroscopy.

INTRODUCTION

Carbon nanotube (CNT) technology is developing very fast leading to decrease in the dimensions of devices used in today’s technological applications, such as sensors, transistors, field emitters, flat panel displays, catalyst [1-4], etc. CNT is a tubular structure made of carbon atoms, having diameter of nanometer order but length in micrometers. This kind of structures was synthesized and studied by several researchers [5-10]. For the first time, Iijima’s evaluated detailed analysis of helical arrangement of carbon atoms in 1991, proved to be a discovery report [11]. Since then, CNT has remained an exciting material ever. Its so-called extraordinary properties: many-fold stronger than steel, harder than diamond, electrical conductivity higher than copper, thermal conductivity higher than diamond, etc. The most common methods used for the production of CNTs are laser vaporization [12], arc discharge [13], and catalytic chemical vapor deposition (CVD) [14]. As compared to arc-discharge and laser-ablation methods, CVD is a simple and economic technique for synthesizing CNTs. Arc- and laser-grown CNTs are superior to the CVD-grown ones in crystallinity, however, in yield and purity, CVD overcome the arc and laser methods. This method enables the use of various substrates, and allows CNT growth in a variety of forms, such as powder, thin or thick films, aligned or entangled, straight or coiled nanotubes, or a desired architecture of nanotubes on predefined sites of a patterned substrate [11]. Therefore, among several techniques of CNT synthesis available today, chemical vapor deposition (CVD) is most popular and widely used because of its ease of scale-up and low set-up cost, and particularly high production yield [11]. In addition to synthesis method, the properties of the CNTs are influenced with the different growth condition such as the feedstock pressure, the catalyst particle size, production temperature, and substrate properties and growth time [15-19]. Recent studies showed
that 26-28 the diameter is increase with time due to expand of nanocrystalline carbon or glassy carbon sheath [17]. Also there were some reports indicating that the growth at higher temperatures yields thinner and longer CNTs in methane (CH$_4$) CVD [18].

Evaluate the effect of various growth conditions on the quality of the synthesized carbon nanotubes is difficult, costly and time consuming. Therefore, provide a good model to study the effects of different conditions on the quality of the synthesis of nanotubes is necessary. Most systems are extremely difficult and time demanding to model by accurate mathematical equations due to the complexity of the system structure, nonlinearity and uncertainty [20]. Hence, traditional modeling approaches are not usually capable of predicting system’s performance correctly. Furthermore, intelligent techniques (i.e. neural network, fuzzy logic) are often practical for developing an accurate model without requiring any explicit mathematical representation [21, 22]. An adaptive neuro-fuzzy inference system (ANFIS) integrates fuzzy logic system with neural network to exploit the capability of each other. In fact, An ANFIS is constructed so that membership function parameters of the fuzzy system are tuned using the learning algorithms of the neural network. Therefore, the ANFIS architecture can successfully predict the nonlinear behavior of systems with acceptable accuracy [23].

Herein, we report the synthesis of CNTs through CVD method over Co-Mo/MgO catalyst, and methane as a carbon source. We focused on the influence of the temperature, amount of H$_2$O, and reaction time on the quality ($I_D/I_G$) of CNTs. $I_D/I_G$ is the intensity ratio of the Raman D-band to G-band is often used to estimate the density of structural defects in CNTs, providing a relative measure for the structural quality of a sample. Thus, in the current investigation, an adaptive neuro-fuzzy based inference system is employed to model the behavior of the CNTs quality ($I_D/I_G$) in presence of three input parameters (i.e. temperature, reaction time and amount of H$_2$O).

**EXPERIMENTAL**

**Materials**

Magnesium oxide, cobalt nitrate, and Ammonium heptamolybdate are all provided by the Merck Chemicals Inc. CH$_4$ gas is provided by Roham Gas Corporation.

**Chemical Vapor Deposition (CVD)**

Chemical vapor deposition (CVD) is the most popular method of producing CNTs nowadays. In this process, thermal decomposition of a hydrocarbon vapor is achieved in the presence of a metal catalyst. The simple schematic of CVD set up is shown in Fig. 1.

**Catalyst preparation**

The catalyst was prepared by loading %10 wt of Co and %2 wt of Mo on MgO as support. In a typical route, appropriate amounts of Co(NO$_3$)$_3$ and (NH$_4$)$_6$Mo$_7$O$_{24}$ were dissolved in 100 ml of methanol and 1 g of substrate was added to this solution.
The final mixture was stirred for 2 h and then the solvent was evaporated by rotary and finally dried at 140 °C for 8 h. The final product was calcined at 450 °C for 5 h. CNTs synthesis was carried out using a controlled amount of water vapor in a fixed bed flowed reactor, which was composed of a ceramic boat containing 0.4 g of the catalyst placed in a horizontal quartz tube. After purging with argon for 30 min, the methane stream was opened for 1-30 min with the rate of 50 ml/min. The decomposition of methane was carried out at 850-1200 °C.

Characterization
The synthesized sample was characterized through the TEM (apparatus model: Zeiss EM 900), SEM (apparatus model: ZEISS, SIGMA Series equipment), Raman spectrometer (apparatus model: SENTERRA- BRUKER (Germany)), and XRD (apparatus model: Siemens, model D5000).

Adaptive neuro-fuzzy inference system (ANFIS)
An adaptive neuro-fuzzy inference system (ANFIS) is a hybrid intelligent system which uses the learning ability of the neural network with the knowledge representation of the fuzzy logic [24]. The architecture of ANFIS model with 2 inputs \((x_i, x_j)\) and one output \((\phi)\) is shown in Fig. 2.

As can be seen from Fig. 2, the ANFIS architecture contains of five layers feed forward neural network which are explained as follows:

- **First layer**
  This layer is named as an input layer. Each neuron in this layer saves the parameters of the membership function and crisp inputs are converted to membership degree values which change between 0 and 1. The output signals of this layer are calculated by:
  \[ O^i_k = \mu(x_i) \]
  \[ i = 1,2,...,I \quad j = 1,2,...,N \quad k = 1,2,...,N \times I \]  \(1\)
  where, \(\mu\) is the membership degree. As can be seen in equation \(1\), the number of neurons in this layer is equal to the product of number of inputs \((N)\) and number of fuzzy rules \((I)\).

- **Second layer**
  Each neuron of this layer performs a connective operation (i.e. “AND”) to calculate the firing strength of a rule. The number of neurons in this layer is equal to the number of fuzzy rules.
  \[ O^2_k = W_k = \prod_{j=1}^{N} \mu(x_j) \quad k = 1,2,...,I \]  \(2\)

- **Third layer**
  A normalization process is performed by the neurons of this layer. The normalized firing strength is calculated by:
  \[ O^3_k = \frac{w_k}{\sum w_k} = \bar{w}_k \quad k = 1,2,...,I \]  \(3\)

- **Fourth layer**
  The normalized firing strength is multiplied by a linear combination of the inputs (i.e. Takagi–Sugeno fuzzy rule) in order to obtain a rules layer.
  \[ O^4_k = \bar{w}_k (p_1x + q_1y + r_1) \quad k = 1,2,...,I \]  \(4\)
  Where, \(p_1, q_1, r_1\) are adaptive parameters of this layer and are called as consequent parameters.

- **Fifth layer**
  The last layer of the network is the weighted average of the outputs of fourth layer [25].
  \[ O^5 = \phi = \sum_k O^4_k \quad k = 1,2,...,I \]  \(5\)
  All the above computation of the ANFIS model is performed by using MATLAB Fuzzy Logic Toolbox.

**Statistical analysis**
Two statistical criteria including correlation coefficient \((R^2)\) and mean square deviation (MSD) are employed for assessing the performance of the developed model in this study. These are defined as:

\[ R^2 = \frac{\sum_{i=1}^{N} (V_{exp} - V_{exp})^2 - \sum_{i=1}^{N} (V_{cal} - V_{exp})^2}{\sum_{i=1}^{N} (V_{exp} - V_{exp})^2} \]  \(6\)

\[ MSD = \sqrt{\frac{\sum_{i=1}^{N} (V_{cal} - V_{exp})^2}{N}} \]  \(7\)

Where, \(N\) is the number of data point and \(V_{exp}\) and \(V_{exp}\) denote the output value of the model and experimental data, respectively. \(V_{exp}\) is the mean value of the experimental data. The perfect agreement is achieved when \(R^2\) and RMSD are equal to 1 and 0, respectively.

**RESULTS AND DISCUSSIONS**

**Characteristic properties**
XRD analysis was obtained to investigate the crystallinity and structure of the samples. Fig. 3a exhibits the XRD pattern of the Co-Mo/MgO catalyst after growth of CNTs. Since MgO and CoO have a similar ionic radius, the diffraction peak of CoO could be masked by the peaks of MgO. In addition, one XRD peak appears at 2θ = 26 in the XRD pattern. It can be concluded that
the peak of CNT is overlapped by corresponding peak of Co$_2$Mo$_3$O$_8$. The Raman technique is used in qualitative and quantitative analysis of carbon nanotubes.

The grown CNT were then characterized by Raman spectroscopy as shown in Fig. 3b. The Raman spectrum consists of in plane bond stretching motion of pairs of sp$^2$ hybridized carbon atoms due to the disordered graphite around 1580 cm$^{-1}$ (G mode) and radial breathing modes of A$_{1g}$ symmetry owing to the presence of six fold aromatic rings (two-dimensional hexagonal lattice) at 1320 cm$^{-1}$ (D mode). $I_G/I_D$ ratio reflects the quality of the as synthesized CNTs. Results of Raman spectroscopy showed that the highest quality of nanotubes were obtained at 1000 °C, %1 moisture, 50 ml/min of methane flow and 20 minutes.

The SEM image of prepared composite is indicated in Fig. 4a. The image displays multi-walled nanotubes are produced and their length is within the range of 2 to 6 micrometers. Moreover, the TEM image (Fig. 4b) established that the synthesized CNTs are multi-walled fragments with each tube consisting of 2–3 layers and diameters in the range of 20-60 nm.

![Fig. 2: Schematic architecture of ANFIS model with two fuzzy rules for two inputs and one output.](image)

![Fig. 3: a) XRD patterns of CNTs/ catalyst at 1000 °C, b) The Raman spectra analysis for prepared composite at 1000 and 1100 °C.](image)
Development of ANFIS model

In the modeling study, the experimental data consists of 120 sets which are randomly divided into training (60%), testing (20%) and validation (20%) subsets. Each input of the ANFIS structure contains three fuzzy sets with Gaussian membership function. This function is determined according to the following equation:

$$\mu(x) = \exp\left[-0.5\left(\frac{x-c}{\sigma}\right)^2\right]$$

(8)

Where $\mu$ is the degree of the membership function and $c, \sigma$ are parameters of the membership function. Since several orders of magnitude for input and output variables make the training extremely difficult and increase the learning time, experimental data are normalized between 0.1 and 0.9 by using the following equation:

$$x_{\text{norm}} = 0.8 \frac{x-x_{\text{min}}}{x_{\text{max}} - x_{\text{min}}} + 0.1$$

(9)

In the above equation, $x$, $x_{\text{norm}}$, $x_{\text{min}}$, and $x_{\text{max}}$ indicate the experimental, normalized, minimum and maximum values of data, respectively.

The parameters of these membership functions are given in Table 1. In addition, the some rules used for modeling system as well as the respective membership functions are reported in Table 2.

As mentioned previously, the temperature, the time and the humidity are considered as input variables whereas the output variable is the quality ($I/I_p$) in this investigation.

Performance of ANFIS model

The regression analysis is performed to compare between testing data and predicted values from the proposed ANFIS model (Fig. 5). Obviously, the predicted quality ($I/I_p$) values of CNTs agree with the experimental data quite well with an acceptable correlation coefficient $R^2$ (0.993).

In order to validate the ANFIS model, the
values of quality ($I_O/I_d$) predicted by ANFIS model and experiments with respect to time in various temperatures in the presence of 1% and 2% of $H_2O$ vapor are compared in Fig. 6 (a and b), respectively.

The degree of graphitic crystallinity in the CNT can be estimated qualitatively by calculating the ratio of $I_O/I_d$, where the higher the intensity ratio, the greater the degree of graphitic crystallinity. The highest values of $I_O/I_d$ obtained for CNT synthesized at various temperatures at the 20 min synthesis time are indicated that the growth of tubes at this synthesis times is less defective as compared to those grown at other synthesis time. From $I_O/I_d$ calculation, the CNT synthesized at 900-1000°C has the highest ratio of $I_O/I_d$. This is indicated that the CNTs synthesized at 900-1000°C have better graphite structure than those synthesized at lower and higher synthesis temperatures. The formation of metal carbide that favor high temperature also leads to the lower graphitization of the CNT produced at higher temperature of 1000°C.

These proposed results Correspond with other experimental studies [26]. The growth mechanism of CNTs in CVD has been widely studied. As generally accepted, CNTs are formed by carbon atom dissolving, diffusing, and precipitating through the catalyst droplets in CVD process [27-29]. The dissolving, diffusing and precipitating rates of the carbon atoms are affected by the carbon atom concentration, the temperature and the time of reaction.

At lower temperature, the dissolving and diffusing rates are limited by the low concentration of carbon and with the increase of the temperature; the dissolving and diffusing rates of carbon atoms will increase [26]. In addition, the quality decrease of CNTs with temperatures higher than 1000°C can be explained from two points. First, if the temperature is too high, the chemical reaction between carbon and Co-Mo/MgO catalyst may take place to form Co-Mo carbide leads to lose its catalytic activity for growing CNTs. The Second aspect, the high carbon concentration resulted from high temperature may cause the dissolving rate higher than diffusing and precipitating rates, carbon atoms will accumulate on the surface of catalysts to form a carbon shell, as a result, the catalysts lose their catalytic activity and lead to the lower graphitization of the CNT [26]. Thus, 900-1000°C is the optimum range of temperatures to obtain high quality CNT. MSD from data of Fig. 6 (a and b) is determined 4.4% and this value indicated a significant prediction for the quality ($I_O/I_d$) of CNT process. In order to evaluate the effectiveness of the input parameters on the quality ($I_O/I_d$) of the CNT process, sensitivity analysis is also conducted. Accordingly, the sensitivity of each input is defined as:

$$\text{Sensitivity} = \left[ \frac{\text{% change in output}}{\text{% change in input}} \right] \times 100$$  \hspace{1cm} (10)$$

During the analysis of sensitivity, an input is changed between the mean values ± one
Fig. 5: Comparison of the testing data and predicted result via ANFIS.

Fig. 6: Quality (IG/ID) with regard to reaction time in various temperatures a) in the presence of 1% of H$_2$O vapor, b) in the presence 2% of H$_2$O vapor.

Fig. 7: Sensitivity analysis based on the ANFIS model and the experimental data.
standard deviation, whereas other inputs are held constant at their mean values [30]. Input variables sensitivities on the CNT quality based on the experimental data and the proposed ANFIS model are shown as a graphical bar in Fig. 7. As shown in Fig. 7, the sensitivity results of the developed ANFIS model are similar to the experimental data, with the percent error of less than 5.86%. In addition, the temperature has the maximum percentage effect (94%) on the quality in comparison with other inputs.

CONCLUSIONS

The present study demonstrates the quality variation of CNTs grown by CVD of methane on Co-Mo/MgO catalyst at 850-1200 °C for 1-30 min in the presence of 0-2% of H2O vapor. This study is carried out to investigate the applicability of an adaptive neuro-fuzzy based inference system (ANFIS) approach for modeling the quality of CNTs. This technique is utilized to achieve relationship between three main parameters namely the temperature, the reaction time, and the amount of H2O as well as an output variable, the quality. Results of the ANFIS model illustrate a very good agreement with the measured values for the quality (I/Io) of CNTs (R²=0.99). The sensitivity analysis of ANFIS model parameters indicates that the temperature is the most sensitive to the quality of the CNT process.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

REFERENCES


