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**REVIEW ARTICLE**

# A Study of Catalyst Preparation Methods for Synthesis of Carbon Nanotubes

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**Abstract:** Carbon nanotubes (CNTs) have been rigorously studied during the past decade due to their extraordinary physical, chemical, mechanical, electrical and optical properties and nanosized catalysts plays an important role in the growth rate, purity and structural properties of the CNTs. In this paper we discuss various methods for the preparation of nanosized catalyst particles including electron bombardment, dc-sputtering, and magnetron sputtering, sol-gel and dip dry method in context to CNT synthesis. These methods are presented in a simplified manner so that the mechanism of formation of nanosized material can be illustrated. It is found that physical methods such as electron bombardment, dc-sputtering and magnetron sputtering prepare nanoparticles without any contamination; where as chemical methods such as sol-gel and dip dry methods are simplest and cheapest for the preparation of nanosized catalysts. Moreover, sol-gel method prepares monodisperse catalyst nanoparticles.

**Keywords:** Carbon nanotubes, Nanosized catalysts, Physical vapour deposition method, Magnetron sputtering, Dc-sputtering, Sol-gel method, Dip dry method.

## Introduction

Carbon Nanotubes (CNTs) have attracted scientific interest due to their unique properties[1,2] and potential impact on broad areas of science and technology[3]. Many methods have been used to produce carbon nanotubes such as arc discharge, laser ablation, chemical vapour deposition methods *etc*. Indeed in many synthesis methods for fabrication of carbon nanotubes need nanosized catalyst particles[4].

The unique structures of CNTs endow with various superior properties, for example, low density, very high stability, outstanding tensile strength and resilience, good current carrying capacity and heat transmission ability *etc*.,[5,6]. Due to these interesting properties

CNTs are being investigated for a wide range of applications today. The various applications of CNTs include: electromagnetic and microwave absorbing coatings[7-13], thermal interface materials[14], ionic and electronic transport devices such as actuators[15,16], super capacitors[17], batteries[18,19], fibers[20-27], sensors[28,29], energy storage and energy conversion devices[30-36], radiation sources and nanometer-sized semiconductor devices[37-38], high aspect ratio nanotubes (electrically conductive wire with diameter in nanometer range) are highly desirable as field emission tips for applications such as field emission displays[39-44], X-Ray tubes[45], electron sources for microscopy and lithography[46], gas discharge tubes[47], vacuum microwave amplifiers, scanning probe tips[48,49].

The nanosized catalyst particles provide both nucleation and growth sites for Carbon nanotubes[50]. It has been found that the catalyst nanosized particles play an important role in the rate of growth, purity and structural properties of the carbon nanotubes (CNTs)[51]. The diameter and number of walls of the carbon nanotubes increases proportionally to the size of the catalyst particle[52]. It is worth noting that the catalyst particle size is an important factor in carbon nanotube growth and catalyst with large particle size have been claimed to be ineffective for growth of single walled carbon nanotubes[53,54]. The increase of mean catalyst crystallite size led to decrease of surface area. Lower surface area results in more effective encapsulation with carbon, which decreases the number of free active sites for hydrocarbon decomposition[55]. So catalyst nanoparticle size dictates the structure of the carbon nanotubes.

### *Catalyst preparation methods*

The preparation methods for nanosized catalysts can be broadly classified under the following three categories:

1. Physical Vapour Deposition (Thermal Evaporation) methods
2. Sputtering techniques
3. Chemical methods

### *Physical vapour deposition (Thermal evaporation) methods*

It is the most common technique adopted for the deposition of metal nanoparticles on a substrate. This involves the evaporation or sublimation of the material. The materials are heated to a very high temperature under high vacuum (pressure of the order $10^{-6}$ to $10^{-12}$ Torr) and the vapours are condensed onto a cooler substrate that yields thin films. The quality and characteristics of the deposit will depend on the rate of deposition, substrate temperature, ambient pressure *etc*. and the uni-formness of the film. Very low pressure is essential requirement for thermal evaporation method because the mean path between collisions become large enough to make the vapour beam arrive at the substrate unscattered. Further it reduces the contamination probability of the deposited film. The film is then sintering at a grown temperature to grow nanoparticles on the substrate. The thickness of the catalyst film, temperature or annealing time, generally controls the size of the catalysts. The schematic diagram of physical vapour deposition technique (Thermal Evaporation) is shown in Figure 1.

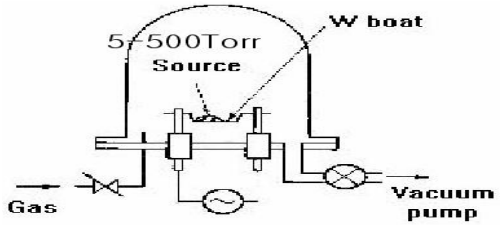


**Figure 1.** Schematic diagram of physical vapour deposition technique

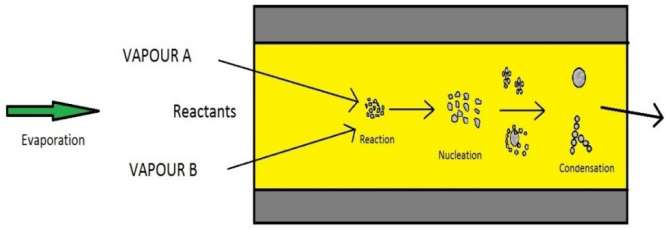


**Figure 2.** Reaction mechanism for preparation of crystalline nanosized particles by thermal evaporation

Figure 2 shows that the thermal decomposition of the catalyst molecule resulted in the formation of supersaturated vapour in a reactor and, subsequently to nucleation and results in a coagulated form. The catalyst particles then grow via condensation, collision and sintering. In order to elaborate the thermal evaporation method below we discuss one of the popular methods:-

### *Electron bombardment heating*

The electron bombardment arrangement consists of a heated material *e.g*. tungsten (W) filament to supply electrons which are accelerated by applying a positive potential to the material for evaporation. The electrons lose energy in the material very rapidly and the range of the energy loss is determined by their energy and the atomic no. of the material. The atoms of the material becomes in a molten form and the evaporated atoms get deposited on the substrate.

Preparation of nanosized nickel (Ni) catalyst particles on silicon oxide surface by electron bombardment technique. A 100KW electron beam accelerator of ELV type whose special features are high electron energy approximately 1.4MeV which extract the electron beam into the target atmosphere. The beam power density as high as 5MW/cm$^{-2}$, makes suitable evaporation of Ni material with vaporization temperature 550 $^{0}$C under atmospheric condition 10$^{-5}$ Torr. The evaporated Ni material then deposits on the silicon oxide surface in a thin film form. After that samples are annealed in a furnace in a nitrogen atmosphere at 740 $^{0}$C for 15-45 min. This process results in formation of nanosized Ni-particles on the substrate.

### *Sputtering techniques*

The ejection of atoms from the surface of a material by bombardment with energetic particles is called sputtering. The ejected or sputtered atom can be condensed onto a substrate. The number of atoms a material ejected for arriving particles is referred to as the sputtering yield. The sputtering yield increases with increasing energy of ions, mass of bombarding ions and with the decrease of angle of incidence on the target. The sputtering technique can be achieved mostly by the following two techniques.

### *DC-diode sputtering*

In DC diode sputtering, the ejection of atoms takes place from the cathode surface by impinging energetic ions of noble gases such as He, Ar, Ne, Kr *etc.* at a reduced pressure under a high dc voltage. DC-diode sputtering is used to sputter a metal material.

Preparation of iron (Fe) catalyst on $SiO_2$ substrate by the dc diode sputtering technique has been described by Faisal *et al*. [56]. In this preparation a silicon substrate is

cleaned in acetone of 100 mL and put in a digital ultrasonicator with de-ionized water at 40 $^0$C for 10 minutes, ultrasonicate with alcohol for 5 minutes, and then rinsed with distilled water. The substrate is then dried in dry nitrogen atmosphere, after that the substrate is put into a reactor at temperature 900 $^0$C and pure oxygen is injected into the reactor for about 20 min. The furnace is then turned off to cool the substrate, which results in deposition of a thin layer of $SiO_2$ on it. Now a Fe catalyst particle is deposited on the $SiO_2$ using dc diode sputtering chamber. In this study the chamber is cylindrical in geometry made of quartz, 3 mm in thickness and covered with two aluminum discs sealed with o-rings. The overall inside dimensions of the chamber is 15 cm in height and 10 cm in diameter. High voltage dc power supply with regulated voltage range from 0-2500 V and current up to 250 mA is used for plasma generation. The plasma sputters the target material (Fe) and deposits the sputtered material in thin film form on the substrate. The film is then sintering and results Fe nanoparticles on the $SiO_2$ substrate.

### *DC Magnetron sputtering*

In magnetron sputtering a magnetic field is introduced such that the sputtering can be done at lower pressure. DC Magnetron Sputtering is most important technique for the preparation of catalyst nanoparticles.

Preparation of cobalt (Co) on Si substrate by dc magnetron sputtering technique was described by Aksak *et al.*[57]. In this report the researchers used AJA ATC Orion 5 UHV sputtering system with four 2-inch magnetron heads for deposition of catalyst thin film. The system includes a substrate holder which is able to rotate, a heater, and a load-lock chamber and the chamber base pressure is $10^{-6}$ Torr before the catalyst film growth. The substrate is cleaned chemically in methanol for 15 min, ultrasonicate for 14 min and then rinsed with distilled water, the substrate is then loaded into the growth chamber and pre-sputtered the target for 1 min. The distance between substrate and target is 7cm with a dc sputtering at 20 W, pressure 0.5 mTorr and a growth rate 0.1 A$^0$/s. A thickness monitor is used to measure the catalyst film thickness and then the sample is cut into small pieces before the carbon nanotubes growth.

### *Chemical methods*

In this method chemical compound molecules are taken in two groups. The first group is gas phase to transport volatile molecule to the surface serving as a substrate and the second group uses the liquid phase as the mass transfer media. In both cases molecules of chemical compounds serving as precursors are delivered to the substrate surface and chemically modified to obtain the desired nanoparticles. The chemical methods are very important for the growth of catalyst nanoparticles. The two techniques involved in chemical methods are as follows:

### *Sol-gel technique*

In sol gel technique materials are formed in gel type solution. Sol-gel method has been extensively used in the preparation of metal catalysts because it results in highly homogenous materials with high degree of metal dispersion and results in monodispersed nanoparticles. In 2005, Perez-Mendoza *et al.*[58] prepared cobalt catalyst by the sol-gel method using MgO as catalyst support. In this study citric acid was mixed with $Mg(NO_3)_2.6H_2O$, the nitric salt of the active metal cobalt, few milliliters of distilled water and the mixture was stirred for formation of clear solution. The solution was then dried at 393K into a foamy paste and then calcinated in air atmosphere at 1023 K. The whole process results in nanosized cobalt catalyst particles.

*Dip dry technique*

In dip dry technique the growth of catalysts nanoparticles on either metallic or non metallic substrates is obtained by dipping them in appropriate solutions containing metal salts without the application of electric field. This is one of the cheapest and simplest techniques. In 2013 Lal *et al*.[59] prepared iron catalyst nanoparticles from aqueous solution of $FeCl_3$ on silicon substrate by dip dry method. In this preparation 2 mg of $FeCl_3$ salt (precursor) is dissolved in 27 mL of distilled water, until a clear solution is formed. The silicon substrate is dipped in aqueous $FeCl_3$ solution and heated at 100 $^0$C temperature in the oven, after that the samples are dried and a thin film of $FeCl_3$ is formed on the substrate.

## Conclusion

We have illustrated physical and chemical methods to prepare catalyst nanoparticles that play an important role in controlling the structures of carbon nanotubes. Physical methods synthesize pure nanosized catalyst particles due to presence of vacuum system. The sputtering technique takes less time but high voltage than thermal evaporation for the growth of nanosized catalysts. Chemical methods are simple and low cost techniques for preparing of nanoparticle catalysts. Furthermore, it is concluded that sol-gel method is simple and prepare monodisperse nanoparticles, which have variety of potential applications for the synthesis of carbon nanotubes.

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