Synthesis of multi-walled carbon nanotubes by thermal CVD technique on Pt–W–MgO catalyst

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1. Introduction

The discovery of the carbon nanotubes (CNTs) by Iijima [1] has been the breakthrough in nanotechnology keeping in view their potential applications in different fields. The unique electrical and mechanical properties of the CNTs, young’s modulus and the tensile strength [2] among all the so-far explored materials are what make CNTs one of the best candidates for the development of high strength composite materials [3]. So far, different methods have been utilized to synthesize and explore these extra ordinary materials of interest; however, the most common method for the development of CNTs is chemical vapour deposition (CVD) because of the fact that it results in a higher yield content and the quality of CNTs it produces [4,5].

For the preparation of CNTs by CVD, the initial step involves the thermal decomposition of hydro-carbons (in our case methane) so as to liberate the carbon which finally deposits over the catalyst. The catalyst plays a key role in the synthesis of CNTs owing to its ability to catalyse the activity of the reaction and to provide the surface area for the adsorption of the carbon [6]. Most commonly used catalysts in CVD are Fe [7,8], Co [9], Mo [10], and Ni [11,12], but recent works have revealed that the bi-metallic and tri-metallic catalysts can also favour the reaction and have certain advantages [13]. In fact, the combination of various catalysts proves out to be more beneficial for quality and yield as well [14]. For example, Rh–Pt catalyst produced narrow diameter distribution of CNTs [15], Fe–Mo catalyst produced the highest crystallinity CNTs [16], Ni–Al produced a positive change in the yield of MWCNTs [17], Ni–Co catalysts supported on TiO2 for use in CVD depicted a positive response in growth process of nanotubes [18], whereas a synergistic effect was observed on the growth of CNTs using Fe–Co catalyst [19]. Likewise, Co–W also influenced the growth in case of an arc discharge method [20]. All the above-cited papers [13–20] along with other studies [20–25] report the use of bi-metallic catalysts for synthesizing nanotubes for the better reason of improved quality, yield and at the same time keeping in view the potential applications of the as-prepared nanotubes.

Tungsten, as that of Mo, possesses a mixed behaviour towards the growth of CNTs [26]. Researchers have obtained functionalized structures by the growth of WO3 on CNT templates which can be used as gas sensors, catalysts and electrochromic devices [27]. On the other hand, a narrow diameter distribution CNT growth was reported using platinum catalyst as compared to cobalt [28]. Therefore, keeping in view the importance and advantages of the tungsten and platinum in CNT growth, here in this study we first...
time report the synthesis of MWCNTs on Pt–W catalyst using MgO as a support for the reason that it can be easily removed [29]. The growth of the MWCNTs was confirmed by field emission scanning electron microscope (FESEM), high-resolution transmission electron microscope (HRTEM) and Raman Spectroscopy.

The paper is organized as follows: Section 2 describes the experimental details, and Section 3 presents the results and discussions. The conclusion remarks are presented in Section 4.

2. Experimental details

In the CVD synthesis of the CNTs, the first step is the preparation of catalyst. Here, we prepared the catalyst by dry impregnation method [30]. In a typical catalyst preparation, Na₂WO₄·2H₂O (2.2 mmol), K₂PtCl₆ (0.056 mmol) and Mg(NO₃)₂·6H₂O (50 mmol) were dissolved in 72 mL of methanol under sonication for 50 min. After that, the solution was refluxed at 90°C in magnetic stirrer for a period of 5 h which allowed the formation of dry mixture and the volatile impurities to escape out. The additional amount of moisture was removed by allowing the mixture to dry overnight in hot air oven. Finally, the mixture was taken out and crushed in the mortar and pestle so as to reduce the particle size.

The as-prepared catalyst was put in a quartz boat distributed evenly and placed in the furnace of the thermal CVD system (TechnoS Instruments). The growth of the CNTs in the furnace took place in four steps. At first step argon (500 sccm) was passed into the furnace with the temperature reaching up to 800°C in 3 h. After the above process completes, hydrogen (300 sccm) along with argon (500 sccm) was allowed to pass into the quartz tube keeping the temperature constant at 800°C for a period of 1 h. During the next half an hour, methane (50 sccm) as carbon source and argon (200 sccm) were passed into the furnace, while during the final step, argon (500 sccm) was passed for a period of 3 h during which the furnace was allowed to cool down to the initial temperature (room temperature). The high temperature of the furnace results in the pyrolysis of methane gas yielding out carbon, which finally gets deposited on the catalyst mixture resulting in the formation of MWCNTs.

3. Results and discussions

Figure 1 shows the XRD pattern of the as-prepared catalyst using Bruker D8 Advance X-ray diffractometer. The X-rays of wavelength 0.154nm (Cu K-alpha) were detected using a fast counting detector based on silicon strip technology (Bruker Lynx Eye detector).

The XRD analysis reveals the presence of tungsten, platinum as well as magnesium oxide in the as-prepared catalyst. The peak at 2θ = 36.00°, 58.65°, and 73.11° corresponds to tungsten (space group: 1–3 m (229), a = 3.155 Å, d = 2.2600, 1.5800, 1.2900), whereas peaks at 2θ = 40.46° and 2θ = 42.84°, 62.35°, 74.65°, 78.84° correspond to platinum (space group: Fm-3m, a = 3.92000 Å, d = 2.2632) and of support magnesium oxide (space group: Fm-3m (225), a = 4.203 Å, d = 2.1000, 1.4800, 2.4200, 1.2100), respectively.

We employed Raman spectroscopy using a LARAM-HR Raman spectrometer at a wavelength of 488 nm (argon laser) to investigate the structural formation of as-grown CNTs. The Raman spectra of the sample (Figure 2) show that two high intensity peaks at 1349 cm⁻¹ correspond to defect-induced band (D band) and at 1594 cm⁻¹ correspond to graphene mode (G band) well known for MWCNTs [31]. The ratio of the intensities of the D and G bands (I_D/I_G) showed a value of 1.1 which is consistent with the earlier reported results [32]. The RBM mode (120–300 cm⁻¹) is absent in our spectra which confirms that the grown CNTs are MWCNTs and not SWCNTs. These results are also confirmed by FESEM and HRTEM micrographs.

Figure 3 shows the FESEM micrographs of the as-grown CNTs and from these images, it is quite clear...
that a network of CNTs has been formed on the catalyst particles. The quality and crystallographic structure of the as-prepared CNTs are further confirmed by HRTEM (LIBRA 200 TEM, Operating voltage 200 KV) images (Figure 4).

The HRTEM images (Figure 4) show that different structures of MWCNTs have been formed besides indicating that some catalyst particles are attached on the surface of the CNTs as they were lifted-off from the MgO support during growth process and integrated on the CNT structure. Furthermore, the mechanism for the growth of the synthesized MWCNTs is expected to be tip growth, which is evident from the HRTEM micrographs wherein the dark spot observed is constituted by catalyst nanoparticle [26]. The structure of the CNTs depends upon the size and density of the catalyst and

![Figure 3](image3.png)

**Figure 3.** (a) low magnification (b) high-magnification FESEM images of as-synthesized MWCNTs on Pt–W–MgO catalyst.

![Figure 4](image4.png)

**Figure 4.** HRTEM images of the different structures of as-synthesized MWCNTs on Pt–W–MgO catalyst (a) straight and coiled (b), (c) open tip and (d) close tip MWCNTs.
their activities during growth process; therefore, the interaction between specific catalyst particles and growing nanotubes gives rise to the formation of different structures of MWCNTs [30,33]; besides, the concept of spatial velocity on extrusion of carbon material from catalyst particles cannot be ignored [34]. Irrespective of arc discharge and laser ablation synthesis of nanotubes, in case of CVD, the growth of nanotubes and nanofibres (bamboo-shaped nanotubes) is often controlled with the size of the catalyst particle [35]. In general, if the catalyst particle density is high and distribution of catalyst activity is broad, straight and waved MWCNTs form [33], whereas helix/coiled MWCNT formation is usually explained on the basis of interaction between the specific catalyst particle and the growing nanostructure [36]. Furthermore, the resulting carbon (product) was weighted and the synthesis yield was 185% with respect to the initial weight of the catalyst.

For CNT material, the thermogravimetric analysis (TGA) has been widely used to quantify the relative amounts of amorphous carbon, CNTs and the catalyst material present in the product synthesized by various techniques [37]. Typically thermal decomposition of the sample in the temperature range 300–400°C were attributed to the removal of amorphous carbon, from 400–700°C oxidation of CNTs and > 700°C for removal of massive graphitic material. The TGA of the sample was carried out with TGA-Q50 from 200°C to 1000°C (refer Figure 5) and is used to determine the state of the catalyst at the end of the synthesis. It is clear from this curve that the sample is of CNT material and contains 12% as catalyst particles at the end of the heating of the sample in air. This shows that the grown product without purification contains catalyst particles which can be removed partly by washing the sample in HNO₃.

The results of this study prove that Pt–W catalyst can catalyse the growth process of CNTs and adds to literature an alternative experimental method for MWCNT growth.

4. Conclusions

This study reports the growth of MWCNTs on Pt–W catalyst at 800°C using the CVD technique. The XRD peak position analysis showed that the as-prepared catalyst contains platinum, tungsten and magnesium oxide. The growth of MWCNTs was confirmed by FESEM, HRTEM and Raman Analysis. The FESEM images reveal that a network of CNTs has been formed with no presence of impurities and catalyst particles. The HRTEM images clearly showed the MWCNT formation with no lateral carbon deposit. Raman analysis showed that the concentration of defects is low in the sample.

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Disclosure statement

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