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Research Article

Synthesis and Optimization of MWCNTs on Co-Ni/MgO by Thermal CVD

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Multiwalled carbon nanotubes (MWCNTs) were prepared by the thermal chemical vapor deposition (CVD) technique. Monometallic and bimetallic Co and Ni combinations were used as a catalyst on MgO support. The mixer of H_2/C_2H_2 was used as a carbon source. The prepared CNTs were found to possess different shapes, morphologies, and sizes. Maximum yield was found for 50% Co (MgO: 50% and Ni: 0%) catalyst at 600°C. Scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) techniques were used for structural analysis. Raman spectra were taken to investigate the quality and crystalline perfection of the prepared CNTs. The ratio of D- and G-bands (I_D/I_G) was measured from these spectra.

1. Introduction

Carbon nanotubes (CNTs), discovered in 1992 by Iijima [1], are tiny, hollow tubes made of pure carbon just a few nanometers in diameter and up to few hundreds microns in length. Since the discovery of carbon nanotubes, researchers were attracted to work on these fascinating materials. Carbon nanotubes exhibit unique electrical properties, efficient heat conductivity, and excellent mechanical strength. Due to their outstanding physical properties, CNTs are one of nanotech's most promising molecular building blocks. CNTs have recently emerged as an attractive cold cathode material due to their excellent field emission properties such as low turn-on field, high current density, and long-term stability [2]. The other forms of carbon nanostructures, such as the carbon nanofibers (CNFs) [3] and carbon nanoparticles (CNPs) [4], also have excellent electron emission characteristics. Carbon nanotubes imagined to be made out of a slice of a graphite monolayer, which is rolled up into a seamless cylinder. Three electrons per carbon atom are used for covalent bonding in sp^2 hybridization, while the forth electron is smeared out over the wire-like structure and supports current transport along the carbon scaffold. Due to the one-dimensional nature of the CNT, scattering is absent at moderate current densities giving rise to ballistic transport. As a consequence, the current density in CNTs can be a factor of 10^2–10^3 higher than in metals. Nanostructured graphitic materials such as single-wall carbon nanotubes (SWNT) and multiwalled carbon nanotubes (MWNT) [5], fullerenes, onion-like carbon, and related structures [6] are mainly obtained by evaporating solid carbon targets by means of arc-discharge and laser ablation.

Several methods have been employed for the synthesis of CNTs, which include arc discharge, laser ablation, plasma-enhanced chemical vapor deposition (PECVD) and thermal chemical vapor deposition (CVD). Thermal chemical vapor deposition (CVD) is a most promising synthesis approach in view of the lower temperatures requirement, good control of deposit morphology, capability of scaling up the process [7, 8]. Various monometallic and bimetallic catalytic systems with different supports have been explored for the production of CNTs. The Fe/MgO, Co/MgO, Fe/Al_2O_3, Fe-Mo/MgO, Co-Mo/MgO, and $Co\text{-}Ni/SiO_2$ catalysts have produced different types of CNTs ranging from SWNT, DWNT, and MWNT [9–12]. It is to be mentioned here that the morphology of the metallic particles deposited on the substrate films are principally depends on the substrate effective resistance [13]. The forms of CNTs produced depend upon

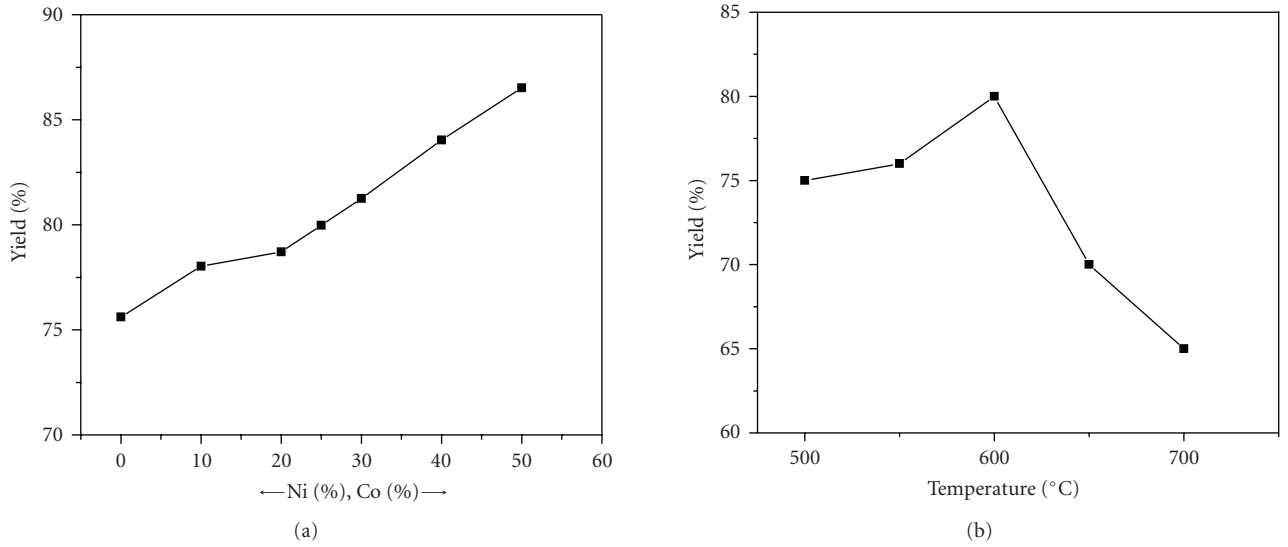


Figure 1: CNT yield as a function of (a) Co-Ni catalysts loading (Wt%) during 60 minutes growth time with flow of H_2 + C_2H_2 (100 + 15 mL/min) at 600°C, (b) reaction temperature of 25% Co + 25% Ni catalyst on MgO support.

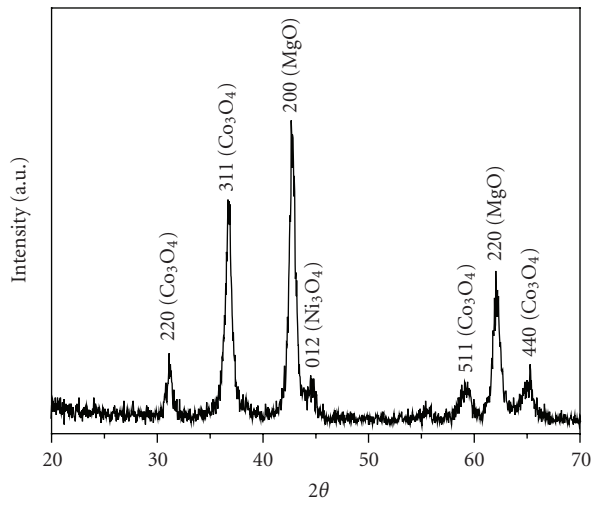


Figure 2: Representative powder XRD pattern for the catalyst 25% Co + 25% Ni on MgO support.

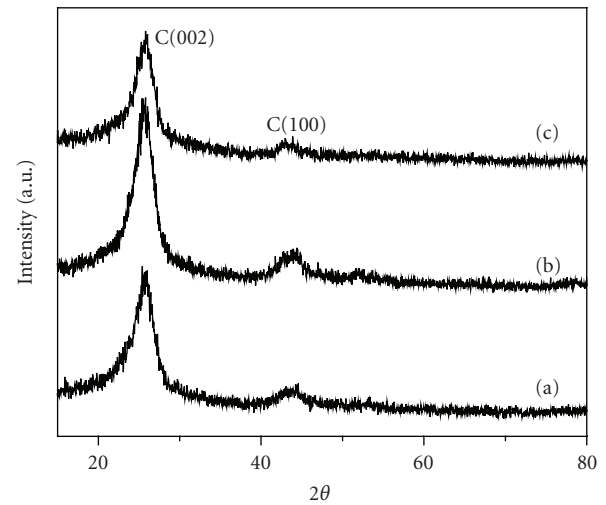


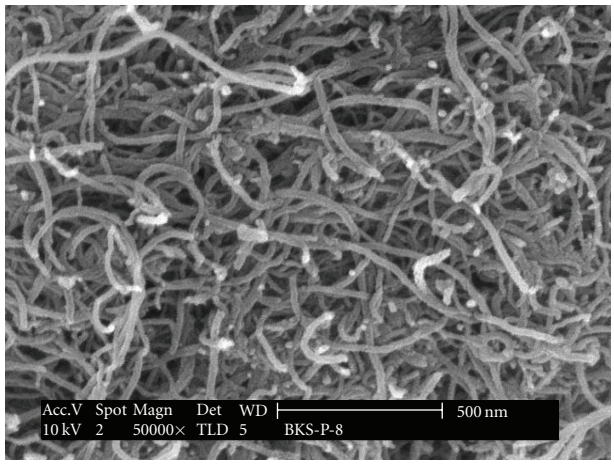
Figure 3: Representative powder XRD patterns for CNTs synthesized using (a) 50% Co, (b) 25% Co + 25% Ni, and (c) 50% Ni on MgO support.

the carbon source and various experimental conditions. The bimetallic catalysts combinations have proved to be better candidates for CNT synthesis. The different process routes can favor the selective production of other curled carbon nanostructures [14–16].

We report results on optimization of Co- and Ni-based monometallic and bimetallic catalytic systems for the synthesis of MWNTs by decomposition of acetylene (C_2H_2). We also correlate the morphology and structural features with the employed catalytic combination.

2. Experimental Details

Thermal chemical vapor deposition (CVD) technique is relatively simple and most common for the commercial production of CNTs. Thermal CVD was employed to synthesize carbon nanotubes using Co-Ni/MgO as a combination of catalyst and support. The high-purity acetylene gas (C_2H_2) was used as a carbon source. Various combinations of metal ions were supported on MgO in order to see their effect on yield and quality of the CNTs. MgO (50%) was kept constant and varying combinations of Ni and Co were tried and investigated. The catalyst ratios were taken as 50% Co, (10% Ni + 40% Co), (20% Ni + 30% Co), (25% Ni + 25% Co), (30% Ni + 20% Co), (40% Ni + 10% Co), and 50% Ni. The nitrates were used for the starting materials as $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$ with $Mg(OH)_2$. Desired stoichiometric amount of nitrates were ground in ethanol in an agate mortar and the resulting slurry was dried at



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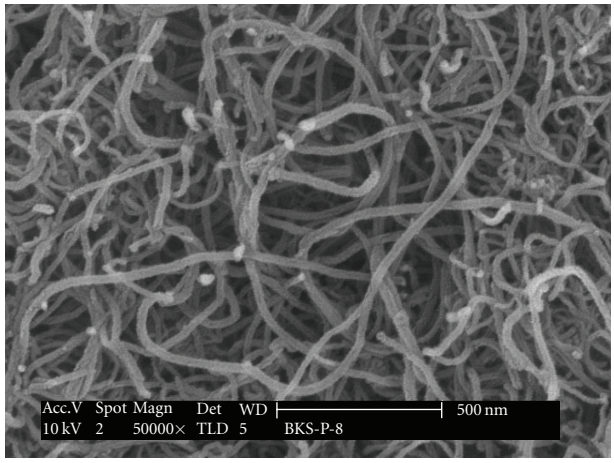

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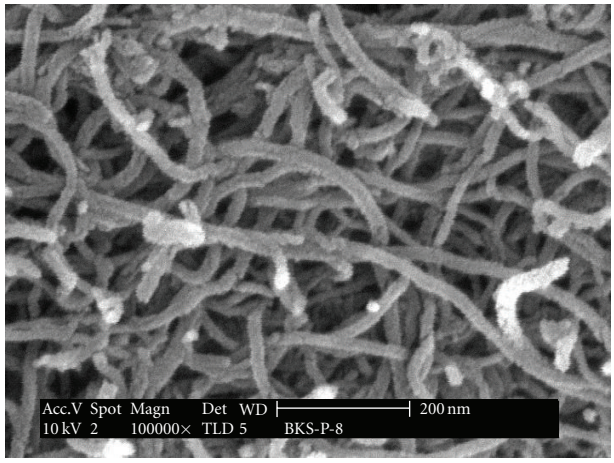
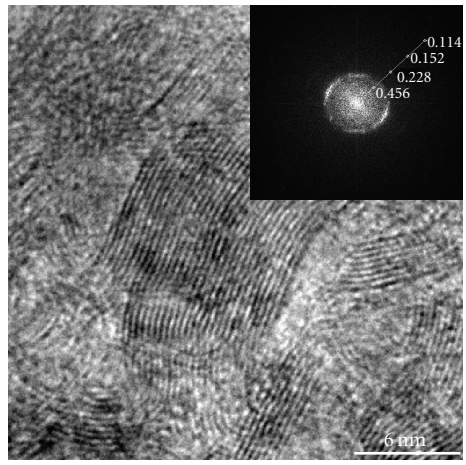


(c)

Figure 4: Representative SEM images of purified MWNTs for (a) 50% Co, (b) 25% Co + 25% Ni, and (c) 50% Ni on MgO support.



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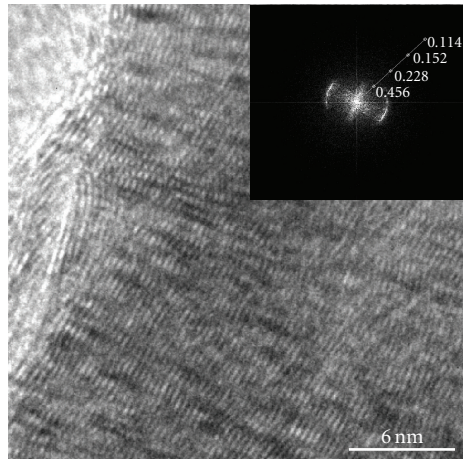

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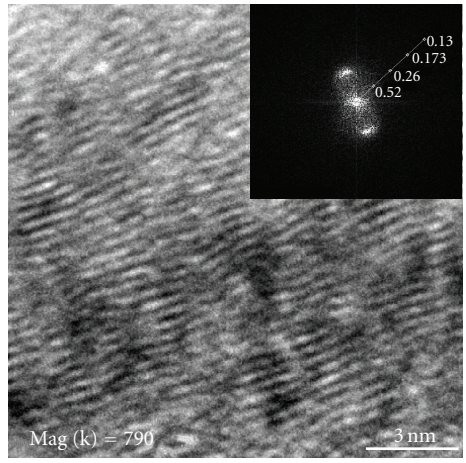

(c)

Figure 5: Representative TEM micrographs for CNTs grown with (a) 50% Co, (b) 25% Co + 25% Ni, and (c) 50% Ni on MgO support.

100°C for 10 hours in an oven. The as-prepared catalyst powder (0.1 g) was uniformly dispersed in an alumina boat that was placed in the central region of a horizontal 100 cm long quartz tube furnace with inner diameter of 4.5 cm. The furnace was flushed with argon while it was heated at 10°C/min rate till the desired temperature (~600–700°C)

was attained. After the attainment of desired temperature, H_2 was introduced in the furnace at 100 mL/min rate for 60 minutes so as to generate active Co/Ni nanoparticles on MgO support. With maintaining the hydrogen stream for the desired period, C_2H_2 at 10–50 mL/min rate was introduced for 1 hour while keeping the H_2 flow rate constant.

The prepared CNTs were purified by refluxing them in 3M HNO_3 for 2 hours at 60°C and subsequently stirred in 5M HCl for 6 hours at 120°C. The product was filtered and washed successively with distilled water and isopropyl alcohol. The purified samples were used for structural characterization. Powder XRD, SEM, and TEM studies were done to investigate morphology, shape, size, and crystallinity of the prepared CNTs. Sample for TEM observation was prepared by suspending the CNTs in ethanol by ultrasonification and drying a drop of the suspension on a carbon-coated copper grid. Philips Tecnai G^2-20 (FEI) electron microscope operating at 200 kV was used for TEM experiments. Raman spectrometer (Bruker, FRA106, excitation beam wavelength-1064 nm) was used to confirm the formation of the CNTs.

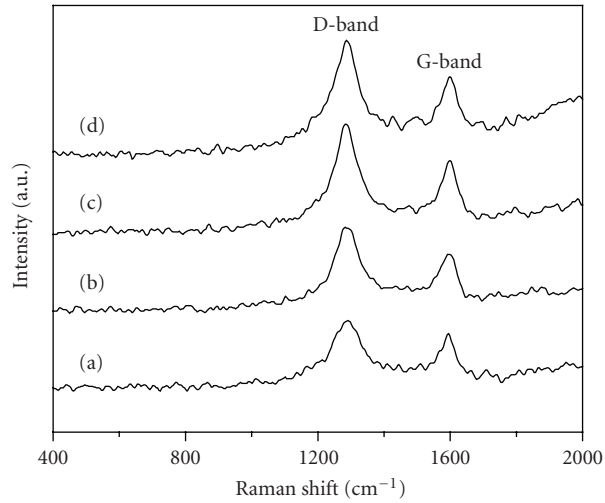

Figure 6: Raman spectra of purified multiwalled CNTs for (a) 50% Co, (b) 25% Co + 25% Ni, (c) 20% Co + 30% Ni, and (d) 50% Ni on MgO support.

3. Results and Discussion

Carbon nanotubes were prepared by thermal chemical vapor deposition method using Co/Ni as catalyst and C_2H_2 as a carbon source. MgO was used as a support for these catalyst nanoparticles. Ni and Co metal ions in various combinations were supported on MgO in order to see their effect on the yield and quality of the CNTs produced. MgO was kept constant at 50% for all the catalyst combinations. We have investigated and optimized the influence of the various experimental parameters such as the reaction temperature, time of H_2 flow for catalyst activation, flow rate of acetylene, and content of the Co/Ni catalyst. Figure 1(a) shows the CNT yield (%) as a function of Co-Ni catalysts loading (Wt%) during 60 minutes growth time with flow of H_2 + C_2H_2 (100 + 15 mL/min) at 600°C. Figure 1(b) shows the representative CNT yield as a function of the reaction temperature of 25% Co + 25% Ni catalyst on MgO support. The yield was calculated from the as-produced CNTs. The CNTs yield (%) was calculated by weighing the sample after the reaction using the following equation:

$$\text{Carbon yield (\%)} = \left[\frac{M_F - M_I}{M_I}\right] \times 100, \qquad (1)$$

where M_F is the total weight obtained after the synthesis and M_I is the weight of the catalyst taken for the synthesis. It was observed that the yield of CNTs increases with increase in Co content in the catalyst. The highest yield was observed for 50% Co (i.e., MgO: 50% and Ni: 0%). However, the optimized temperature for the highest yield was 600°C. It suggests that Co is more effective as catalyst than Ni. The precursor catalyst combinations were investigated for the phase and crystallinity before being used for the CNTs synthesis. Figure 2 shows the representative XRD pattern for catalyst precursor combination 25% Co + 25% Ni prepared at 600°C. XRD pattern exhibits characteristic peaks of MgO support and the oxides of Co and Ni. Peaks for Co and Ni oxides are clearly seen apart from the mean peak for MgO (200) at 42°. This suggests that the temperature, time, and H_2 gas flow rate optimized for the preparation of the precursor is correct. The average sizes of the crystallites of Co/Ni metal were roughly estimated from XRD peak broadening to be 15–20 nm. It is important that complete conversion of oxidic phase into active Co/Ni particles necessarily occur under the influence of acetylene and hydrogen combination [17]. The representative XRD patterns for purified CNTs prepared with different catalyst Co/Ni combinations are shown in Figure 3. The XRD patterns show graphite-like peaks having (002) and (100) reflections at 26° and 44°, respectively. The presence of broad hump at 44° along with C (100) in Figure 3 corresponds to respective metal nanoparticles. In Co-Mo and Co-Ti systems, it was reported that Co center promotes the growth while other metal components are responsible for alignment and thickness of CNTs [18]. In the present investigations, Co alone on MgO shows higher yield than the bimetallic combination of Co/Ni.

Scanning electron microscopy (SEM) was done to investigate morphology and sizes of the synthesized CNTs. Figures 4(a), 4(b), and 4(c) show SEM images of the CNTs grown with 50% Co, 25% Co + 25% Ni, and 50% Ni, respectively. From these micrographs it is observed that the CNTs exhibit different sizes and morphology for different catalyst combinations without any noticeable carbon nanoparticles. CNTs are oriented randomly in the bending and twisting forms of tubes with few visible defects. The samples grown with different composition of catalysts, reveals that the sizes and diameters do not vary much. The average diameter of about ~25–30 nm was estimated from these images.

Transmission electron microscopy (TEM) in high-resolution mode is the best tool to investigate local structure, particle size, and morphology of the material. Crystallinity and morphology of synthesized CNTs was investigated using high-resolution transmission electron microscopic

(HRTEM) images. Figures 5(a), 5(b), and 5(c) show the HRTEM images for the three different catalyst compositions of 50% Co, 25% Co + 25% Ni, and 50% Ni, respectively. Corresponding SAD patterns are inserted in the micrographs. High-resolution images show that prepared CNTs contain large number of isotropic domains of nanocarbon graphite with random orientations of crystal direction having curved graphene sheets. The intershell spacing is found to be 0.34 nm. The selected area electron diffraction pattern (SAED), inserted in Figure 5(a), shows that the bright ring diffraction peak is originating from the (002) graphite plane. Multiwalled character with some structural defects was also revealed from these micrographs for all the catalyst combinations. MWNTs are highly crystalline in nature with long fringes that are oriented parallel to each other as evidenced from the images in Figure 5. A pair of small but strong bright arcs of (002) diffraction indicates the presence of graphene texture along the tube axis. The outer faint ring probably reveals the defects in the graphite layers in the outer walls of CNTs.

The quality and crystalline perfection of the prepared CNTs can also be estimated by Raman spectroscopy [19]. A perfect nanotube would be a cylindrical graphene sheet composed only of hexagons having minimum defects at the tips to form a closed seamless structure. We have investigated the prepared CNT samples by Raman spectroscopy to determine their quality and perfection. Raman spectra for the CNTs for 50% Co, 25% Co + 25% Ni, 20% Co + 30% Ni, and 50% Ni on MgO support are shown in Figure 6. All the spectra have two strong peaks at 1287 cm^{-1} and at 1595 cm^{-1}. These two peaks are designated as the tangential modes of carbon [20]. The first peak corresponds to the defect-induced A_{1g} or D-band. It is associated with vibrations of carbon atoms with dangling bonds in plane terminations of disordered graphite or glossy carbon. This D-band also called as breathing mode. The second peak known as G-band represents the Raman allowed E_{2g} mode of graphite and is related to the vibration of sp^2 bonded carbon atoms in a two-dimensional hexagonal lattice [21]. The ratio of the intensities of D and G bands (i.e., I_D/I_G) is the indirect measure of the crystallite size and crystalline defects in the CNTs. The I_D/I_G ratio in Figure 6, for CNTs with different Co and Ni concentrations was calculated. The ratio calculated was ~1.24, which estimates the crystallite size and relative extent of crystalline defects. The intensity of D-band is higher than G-band indicating that some amount of disordered graphite as defects or amorphous carbon present in the prepared CNTs.

4. Conclusion

Reasonably good crystalline quality CNTs were prepared with different combinations of Co/Ni catalyst on MgO support by thermal CVD. The CNTs synthesized over different catalysts combinations have different sizes/shapes and morphologies with minimal deposition of carbon particles. HRTEM studies have shown that morphological characteristics are catalyst sensitive and the purity and crystallinity depends on combination of the catalyst. The reaction temperature, gas flow rate, catalyst combination, and support are important parameters to be looked into for quality and efficient growth of CNTs. We expect that these results can also be extended to the preparation of metallic nanoparticles on suitable support/substrate apart from the CNTs

Acknowledgment

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References

[1] S. Iijima, "Helical microtubules of graphitic carbon," *Nature*, vol. 354, no. 6348, pp. 56–58, 1991.

[2] W. A. de Heer, A. Châtelain, and D. Ugarte, "A carbon nanotube field-emission electron source," *Science*, vol. 270, no. 5239, pp. 1179–1180, 1995.

[3] Y. Chen, S. Patel, Y. Ye, D. T. Shaw, and L. Guo, "Field emission from aligned high-density graphitic nanofibers," *Applied Physics Letters*, vol. 73, no. 15, pp. 2119–2121, 1998.

[4] K. H. Park, S. Choi, K. M. Lee, S. Lee, and K. H. Koh, "Stable and uniform electron emission from nanostructured carbon films," *Journal of Vacuum Science & Technology B*, vol. 19, no. 3, pp. 958–961, 2001.

[5] R. Saito, M. S. Dresselhaus, and G. Dreesselhaus, *Physical Properties of Carbon Nanotubes*, Imperial College Press, London, UK, 1998.

[6] A. M. Rao and M. S. Dresselhaus, *Nanostructured form of Carbon: An Overview*, Kluwer Academic Publishers, Erice, Italy, 2000.

[7] M. José-Yacamán, M. Miki-Yoshida, L. Rendón, and J. G. Santiesteban, "Catalytic growth of carbon microtubules with fullerene structure," *Applied Physics Letters*, vol. 62, no. 6, pp. 657–659, 1993.

[8] J. H. Huang, S. P. Chen, C. C. Chuang, I. N. Lin, and C. H. Tsai, "Electron emitters synthesized by selected area deposition of carbon nanotubes on silicon substrates," *Diamond and Related Materials*, vol. 12, no. 3–7, pp. 481–485, 2003.

[9] B. K. Singh, S.-W. Cho, K. S. Bartwal, N. D. Hoa, and H. Ryu, "Synthesis of MWNTs using Fe-Mo bimetallic catalyst by CVD method for field emission application," *Solid State Communications*, vol. 144, no. 10-11, pp. 498–502, 2007.

[10] Z. Zhong, H. Chen, S. Tang, J. Ding, J. Lin, and K. L. Tan, "Catalytic growth of carbon nanoballs with and without cobalt encapsulation," *Chemical Physics Letters*, vol. 330, no. 1-2, pp. 41–47, 2000.

[11] Md. Shajahan, Y. H. Mo, A. K. M. Fazle Kibria, M. J. Kim, and K. S. Nahm, "High growth of SWNTs and MWNTs from C_2H_2 decomposition over Co-Mo/MgO catalysts," *Carbon*, vol. 42, no. 11, pp. 2245–2253, 2004.

[12] C. J. Lee, J. Park, S. Y. Kang, and J. H. Lee, "Growth of well-aligned carbon nanotubes on a large area of Co-Ni co-deposited silicon oxide substrate by thermal chemical vapor deposition," *Chemical Physics Letters*, vol. 323, no. 5-6, pp. 554–559, 2000.

[13] L. Nzoghe-Mendome, J. Ebothé, A. Aloufy, and I. V. Kityk, "Role of substrate on topography features of nickel deposited nanostructures," *Journal of Alloys and Compounds*, vol. 459, no. 1-2, pp. 232–238, 2008.

[14] Q. Zhang, L. Yu, and Z. Cui, "Effects of the size of nano-copper catalysts and reaction temperature on the morphology of carbon fibers," *Materials Research Bulletin*, vol. 43, no. 3, pp. 735–742, 2008.

[15] G.-H. Jeong, A. Yamazaki, S. Suzuki, Y. Kobayashi, and Y. Homma, "Behavior of catalytic nanoparticles during chemical vapor deposition for carbon nanotube growth," *Chemical Physics Letters*, vol. 422, no. 1–3, pp. 83–88, 2006.

[16] G. G. Wildgoose, C. E. Banks, and R. G. Compton, "Metal nanoparticles and related materials supported on carbon nanotubes: methods and applications," *Small*, vol. 2, no. 2, pp. 182–193, 2006.

[17] S. Takenaka, M. Ishida, M. Serizawa, E. Tanabe, and K. Otsuka, "Formation of carbon nanofibers and carbon nanotubes through methane decomposition over supported cobalt catalysts," *Journal of Physical Chemistry B*, vol. 108, no. 31, pp. 11464–11472, 2004.

[18] S. Sato, A. Kawabata, D. Kondo, M. Nihei, and Y. Awano, "Carbon nanotube growth from titanium-cobalt bimetallic particles as a catalyst," *Chemical Physics Letters*, vol. 402, no. 1–3, pp. 149–154, 2005.

[19] H. Hiura, T. W. Ebbesen, K. Tanigaki, and H. Takahashi, "Raman studies of carbon nanotubes," *Chemical Physics Letters*, vol. 202, no. 6, pp. 509–512, 1993.

[20] M. M. Shaijumon and S. Ramaprabhu, "Studies of yield and nature of carbon nanostructures synthesized by pyrolysis of ferrocene and hydrogen adsorption studies of carbon nanotubes," *International Journal of Hydrogen Energy*, vol. 30, no. 3, pp. 311–317, 2005.

[21] C. Singh, T. Quested, C. B. Boothroyd, P. Thomas, I. A. Kinloch, A. I. Abou-Kandil, and A. H. Windle, "Synthesis and characterization of carbon nanofibers produced by the floating catalyst method," *Journal of Physical Chemistry B*, vol. 106, no. 42, pp. 10915–10922, 2002.