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Research Article

SEM images of carbon nanotubes (CNTs): effect of voltage and spot size on image resolutions

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Abstract

Scanning electron microscopy (SEM) is a method used to characterize 2D and 3D materials morphologically. It is of great importance with its high resolution, especially in the characterization of nano- and micro-sized materials. In this study, carbon nanotubes (CNTs) were analyzed with SEM, and high-quality images were obtained. With SEM analysis, it can be seen whether carbon nanotubes are formed in a regular structure or not, and whether there are agglomerations or distortions in the structure and could also be utilized to quantify the degree of purity within samples. The diameters of carbon nanotubes can be measured using SEM images. This study obtained the best imaging parameters by taking many SEM images at different magnifications under 3.5 and 7 kV voltage and 2, 2.5, and 3 spot values. The results showed that in the characterization of CNTs by SEM, low spot and low voltage values are more suitable for detailed surface morphology imaging and obtaining high resolution.

1. Introduction

Scanning electron microscopy (SEM) is a microscopy technique that uses electron beams to examine high-resolution images and detailed surface morphologies of samples [1]. Compared to optical microscopy, it is a type of electron microscopy that allows obtaining much higher resolution images thanks to electron beams, and its resolution can vary from 1 nanometer to several nanometers. In this technique a focused electron beam is sent onto the surface of a sample and the surface scans with this electron beam collects the signals coming from the surface with its detectors and converts them into an image. Electrons interact with atoms on the sample surface and produce various signals that can be used to obtain information about surface morphology and composition. There are two main detectors used in SEM for image formation. The first of them is called the secondary electron (SE) detector, the other is the backscattered electron detector. They are the most common detectors used for high-resolution imaging in the SEM measurements. Besides, an energy dispersive X-ray spectroscopy (EDS) detector is used in SEM to examine the surface composition.

SEM is widely used in many disciplines to analyze many different materials [2-5]. It can analyze organic and inorganic substances from nanometer (nm) to micrometer (μm) size [6]. Using SEM, images can be taken from material surfaces with high precision, at a

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magnification of approximately 300.000x, and even up to 1.000.000X magnification in some devices [7]. The magnification ratio of a standard SEM device is between 5x and 300.000x [8]. SEM is also a convenient imaging method during the sample preparation process. It can display conductive, insulating, wet, and dry samples with different properties with a variable pressure system [9]. The size of the samples to be imaged in SEM must be up to 200 mm in diameter and 80 mm in height [10]. Insulating samples are generally examined by coating them with gold [11].

Carbon nanotubes (CNTs) have attracted great attention due to their extraordinary electronic, mechanical, and thermal properties [12-14]. The properties of (CNTs) and devices using (CNTs) directly depend on the nanotube's morphological properties, the nanotube's crystallographic properties, and any defects in the structure [15]. Therefore, the characterization of (CNTs) and the determination of their morphology are important for quality control and use in different applications [16].

SEM images of the carbon nanotube (CNT) samples were taken by scanning the surface with a high-energy beam of electrons [17]. By sending an electron to the specimen surface, several signals can be detected [18]. When the primary electron is sent, high energy backscattered electrons appear and the primary electron can be diffracted with large angles. Secondary electrons are generated when these backscattered electrons emerge from the surface [19]. These secondary electrons have energies between 0 and 20 eV and can be attracted to a highly efficient positively charged detector [20]. Comparing the primary electron number, the secondary electron number is high and increases as the angle φ between the electron beam and the surface normal increases in proportion to $1/\cos\varphi$ [21].

There is a large annular detector below the final lens, facing toward the sample, and this detector can collect a proportion of the scattered electron signal [22]. With increasing atomic number Z of an elemental sample, the scattering of primary electrons increases [23]. Depending on the surface composition and orientation between the electron beam and surface, the backscattered electron signal from a flat, polished sample provides contrast [24].

The resolution of the backscattered electron image is typically in the range between 0.1-1 μm [25], but it is possible to image very finely spaced regions showing compositional contrast at resolutions down to 2-3 nm using high-brightness guns and efficient backscattered electron detectors. A small high-resolution component in the backscattered signal is generated by incident beam electrons being scattered out of the sample very early in their path. The resolution of the whole backscattered signal can be improved by reducing the beam energy but the detectors become less efficient for the lower energy electrons [26], and so this is not appropriate.

In this study, multi-walled CNTs were synthesized by the chemical vapor deposition (CVD) method and then SEM images of these nanotubes were taken under different voltage and spot values. The effects of voltage and spot-on SEM imaging of CNTs were investigated to obtain images of CNTs with high quality and high resolution.

2. Materials and Methods

2.1 CNT Growth Process with Thermal Chemical Vapor Deposition (TCVD) Method

In this study, the TCVD method was utilized to synthesize CNTs (Lindberg/Blue M 1100 ^{o}C Split Mini Furnace) [27]. 50 mg Co-Mo/MgO powder catalyst placed in a quartz boat was transferred into the TCVD system. Initially, a catalyst pretreatment process was carried out under H_2 atmosphere with a flow rate of 200 sccm for 1 hour at 850 ^{o}C to reduce metal

oxide particles and prevent amorphous carbon formation for high-quality CNT growth. After the pretreatment process, the temperature was increased up to 1000 ^{o}C at a rate of 5 ^{o}C/min, and CNT growth was started at 1000 ^{o}C by opening CH_4 gas with a flow rate of 50 sccm. CNT synthesis took 60 min at this growth temperature under 200 sccm H_2 and 50 sccm CH_4 gases at atmospheric pressure.

After the CNT growth process, CH_4 gas was turned off. The system temperature was set to 0 ^{O}C and the system and synthesized CNTs was left to cool under H_2 atmosphere.

2.2 Morphological Characterization of CNTs with SEM

SEM is one of the most widely used tools for analyzing the morphology and size of CNTs in powder form. Its popularity stems from its simplicity and suitability for routine use, offering an advantage over other microscopy methods. SEM can easily be employed to assess the general structure of CNT samples, determine their purity, dimensions, and their orientations [28-30]. Diameters of CNTs also can be measured roughly using SEM results.

In this study, to take SEM images of CNTs, CNTs in powder form were fixed by gluing them to double-sided carbon tape. No coating or pretreatment was applied to image CNTs, and imaging was done as an as-grown form of CNTs. A SE detector was used to image CNTs, and voltage values of 3, 5, and 7 kV and a spot values of 2, 2.5, and 3 were scanned to obtain high-resolution images.

The SEM utilized for this study was a FEI QUANTA 250 FEG. A schematic representation of SEM characterization of CNTs is given in Fig.1.

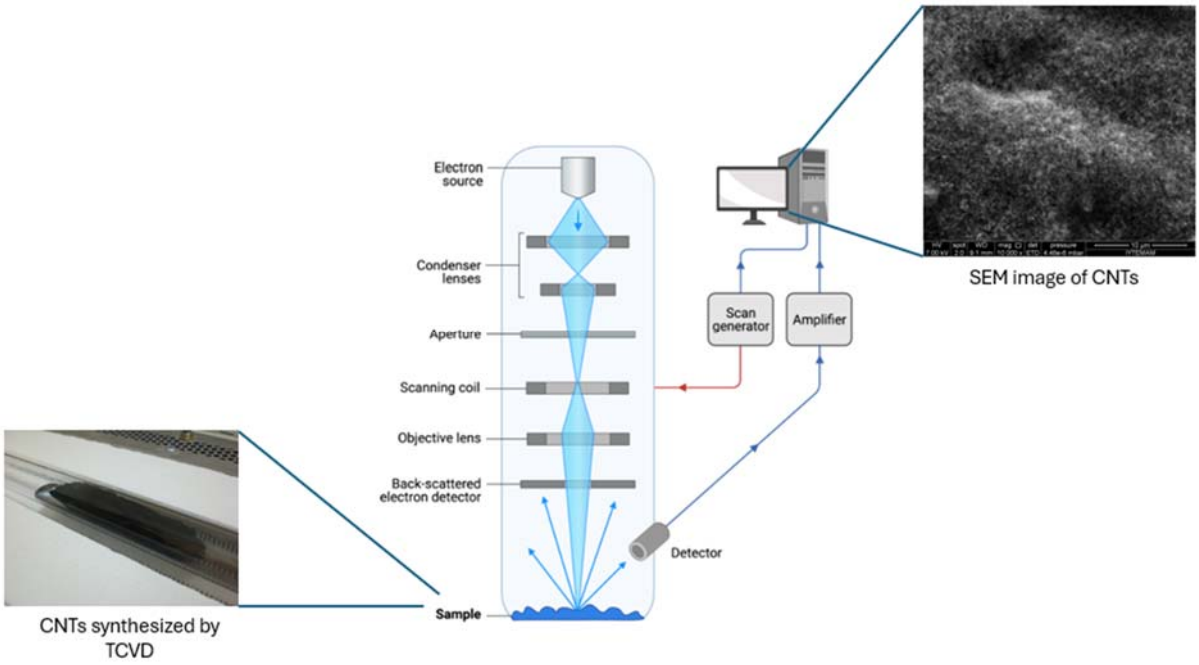

Fig. 1. Schematic representation of SEM characterization of CNTs

3. Results and Discussion

In imaging CNTs in SEM microscopy, the contrast created by the nanotubes provides imaging. The image is formed with the information received from the secondary electrons reflected from the nanotubes and, in some regions, from the catalyst particles remaining during nanotube synthesis [31].

In literature, it is reported that when using tungsten filament SEM, the voltage value should be between 2-10 kV to prevent the sample from charging and to obtain the image of (CNTs) in high-resolution [30]. In the present study, voltage values of 3, 5, and 7 kV were tried obtain high-resolution CNT images.

SEM pictures of the as-grown CNTs taken under 3 kV accelerating voltage at different spot values and different magnifications are given in Fig. 2 and Fig. 3. SEM images of nanotubes showed that CNTs synthesized by TCVD method under H_2 environment were high purity and high quality. SEM images of CNTs were taken at increasing magnifications: 25.000x, 50.000x, and 100.000x. In this way, it is possible to obtain information about the general morphology of the CNT sample and to closely examine the morphology of a single nanotube. General images taken from further away, especially nanotube bundles in the powder CNT sample, can be observed and examined whether they contain irregular structures. The purity level of the nanotubes can be seen. In close-up images taken at 100.000X and higher magnifications, nanotubes can be observed individually and their diameters can also be measured. To obtain an accurate value for diameter measurement, the diameter of at least 50 nanotubes from the same sample must be measured and averaged.

When SEM images taken under 3 kV voltage and 2.5 spot value are examined, carbon nanotube bundles can be clearly observed under 25000X magnification (Fig. 2). As the magnification increases, nanotubes become more evident and nontangled CNTs formed in a regular structure are observed. The image quality at these voltage and spot values was considered suitable for CNT imaging.

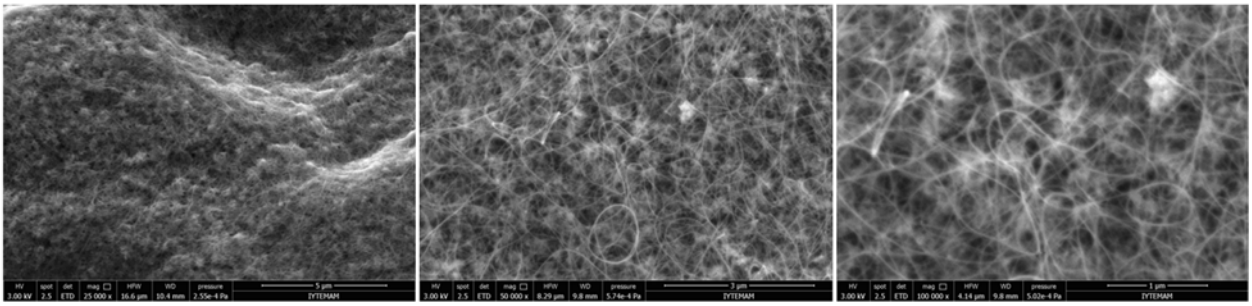

Fig. 2. SEM images of CNTs under 3 kV accelerating voltage, 2.5 spot value at 25.000, 50.000, and 100.000X.

In SEM, spot value refers to the diameter of the electron beam used during imaging. Spot plays an important role in observing resolution and details in SEM imaging. A lower spot value means a thinner, more concentrated electron beam. These results in higher resolution and sharper, more detailed images. Therefore, low spot values are more suitable for observing fine structures, surface features, or small particles. Higher spot values result in a larger diameter electron beam. Under high spotlight, the resolution of the image decreases but increases the depth of field; this can be useful when imaging larger or deeper structures.

When we increased the spot value from 2.5 to 3 while the 3 kV voltage was constant, the contrast between the nanotubes and the ground increased, but it was observed that the depth decreased compared to the SEM images taken under 2.5 spot (Fig. 3).

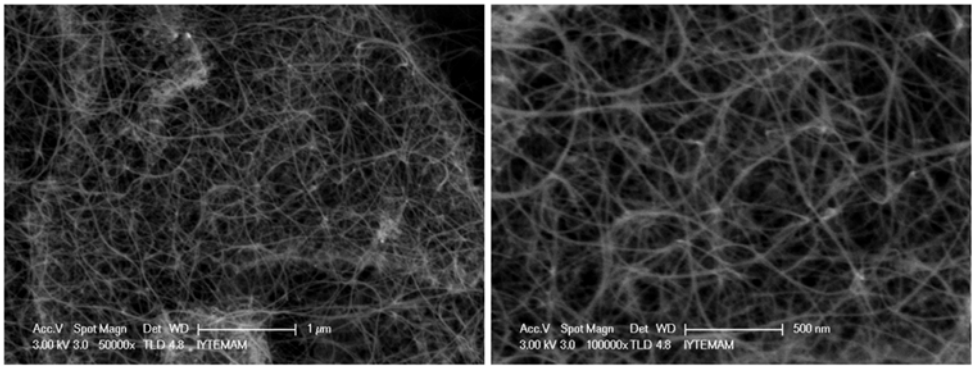

Fig. 3. SEM images of CNTs under 3 kV accelerating voltage, 3 spot values at 50.000, and 100.000X.

In SEM, accelerating voltage is a significant parameter that directly affects imaging. Voltage controls the energy of the electron beam. High voltage increases the energy of the electron beam, which can lead to decreased resolution due to the increased interaction volume of electrons within the sample. Therefore, higher voltage may reduce the resolution of fine details on the surface of the sample.

Lower voltage values result in lower energy electrons interacting more superficially with the sample. The interaction volume is smaller, providing better resolution for surface details. At the same time, lower voltage results in shallower penetration; This is advantageous for surface-sensitive imaging where surface properties are of primary interest.

SEM images taken under 5 kV accelerating voltage at different spot values were given in Fig. 4 and Fig. 5. As expected, it can be seen that SEM images taken under 5 kV voltage provide less detail compared to SEM images taken under 3 kV voltage. Especially in more general images at 25000X magnification, it is seen that the details on the surface decrease and the resolution decreases with the increase in voltage (Fig. 4).

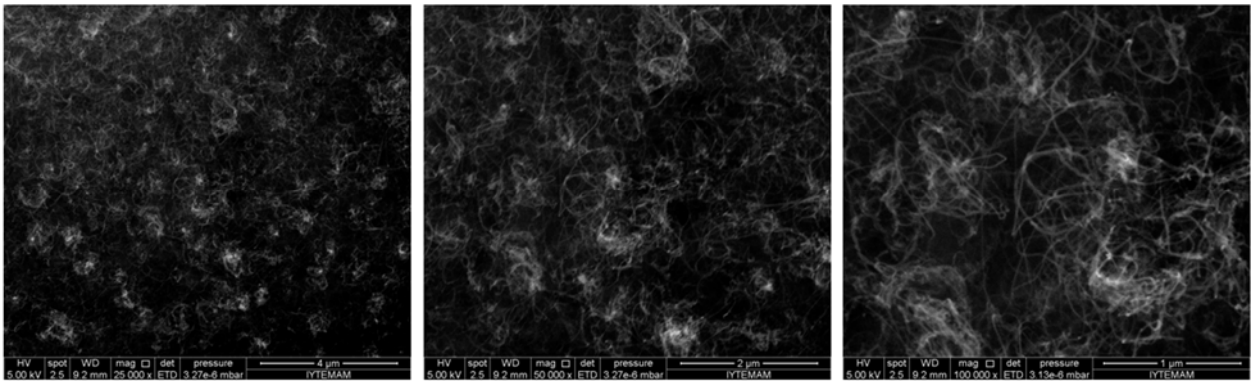

Fig. 4. SEM images of CNTs under 5 kV accelerating voltage, 2.5 spot value at 25.000, 50.000, and 100.000X.

A lower spot size typically results in a weaker signal. Under low spot, the electron beam is focused more into a smaller area, resulting in a lower signal-to-noise ratio. A larger spot provides a larger interaction area, thus increasing the intensity of the signal; this can be useful for capturing clearer images in less time. When the spot value was increased from 2.5 to 3 under 5 kV voltage, it was observed that the contrast increased and the surface details decreased, as in the images taken under 3 kV (Fig. 5).

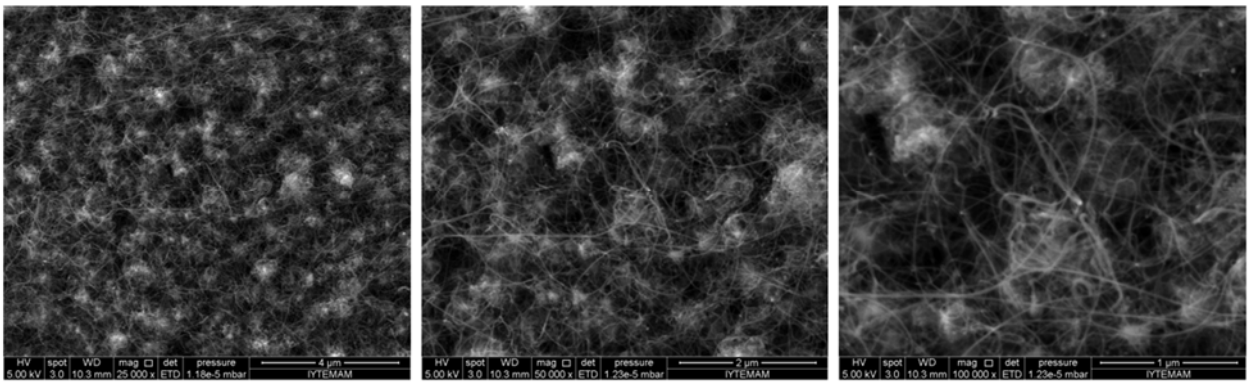

Fig. 5. SEM images of CNTs under 5 kV accelerating voltage, 3 spot value at 25.000, 50.000, and 100.000X.

While it was expected that the details would decrease further at high voltage after the voltage increased to 7 kV, by reducing the spot value to 2, high-quality SEM images of CNTs with high resolution and excellent surface details were obtained. Therefore, the effect of low spot value on image quality is shown in Fig. 6 was also clearly observed.

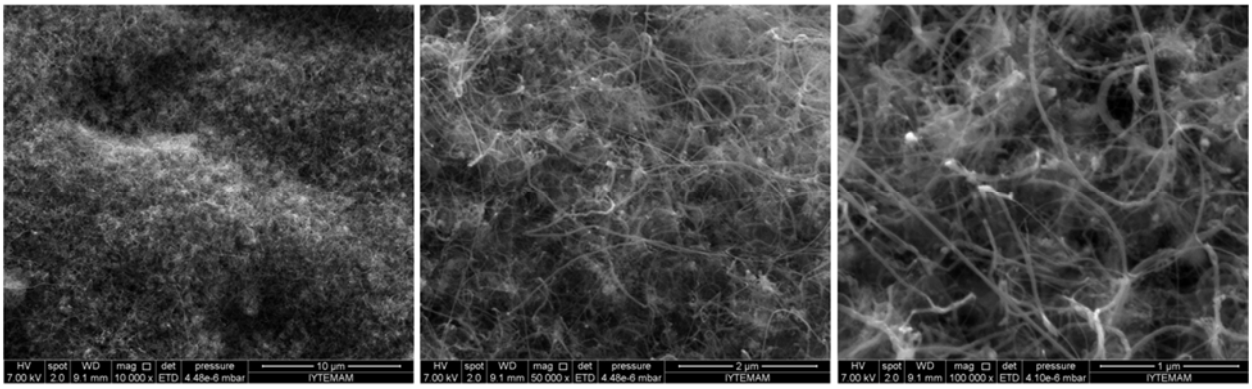

Fig. 6. SEM images of CNTs under 7 kV accelerating voltage, 2 spot values at 25.000, 50.000, and 100.000X.

Since the beam is highly focused on a smaller area with a smaller spot size, it may cause heating in the imaged area and burn in sensitive samples. However, a higher spot value distributes the energy over a wider area, reducing the risk of damage, but reducing image clarity. As a result of the spot value increasing to 2.5 while the voltage remains the same (7 kV), it is seen that there is charging in the regions where the CNT clusters are located, causing excessive brightness. Therefore, CNT clusters cannot be observed clearly (Fig. 7).

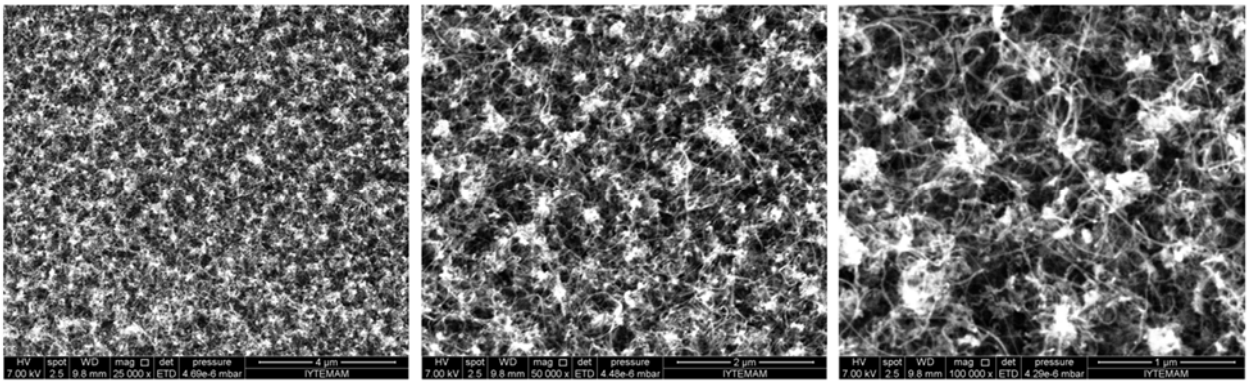

Figure 7: SEM images of CNTs under 7 kV accelerating voltage, 2.5 spot value at 25.000, 50.000, and 100.000X.

Also, using a low spot value may require slower scanning speeds to achieve the same signal strength, potentially increasing imaging time. A larger spot size can speed up imaging due to the stronger signal. Compared to Fig. 7, after the spot value was increased from 2 to 2.5 at 7 kV accelerating voltage value, the charging effect on the image became clear. CNTs are not clearly visible. Even at 100.000X magnification, individual CNTs are very difficult to observe (Fig. 8).

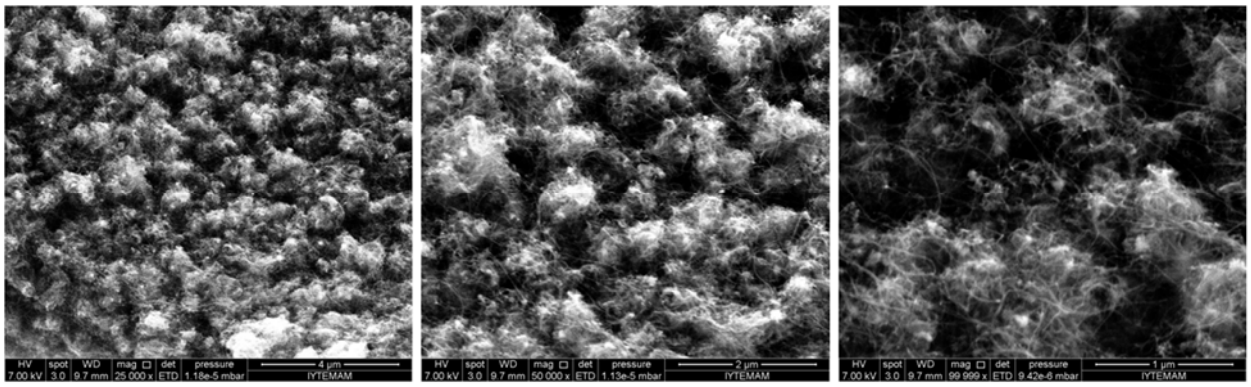

Figure 8: SEM images of CNTs under 7 kV accelerating voltage, 3 spot value at 25.000, 50.000, and 100.000X.

4. Conclusions

In this study, the morphologies of CNTs synthesized by the TCVD method on Co-Mo/MgO powder catalyst were examined by SEM technique. The effects of voltage and spot values at different magnifications were examined to obtain high-resolution CNT images and detailed surface morphology. The results showed that CNTs can be easily imaged in SEM in their as-grown form without any coating.

In SEM imaging, the spot size affects the balance between resolution, signal intensity, imaging speed, and sample preservation. Choosing the optimal spot value depends on the specific requirements of the analysis, such as the level of detail needed and the characteristics of the sample. When the effects of voltage are examined, at high voltage values, electrons penetrate deep into the material surface with their high energy. Therefore, less surface detail can be captured, and more contrast occurs, and very high voltages can damage the sample. At lower voltage values, electrons penetrate the surface less and these voltage values are more suitable for seeing surface details. Therefore, while lower voltage provides higher resolution, it is also less likely to damage the sample. In addition, the choice of voltage and spot values depends on the requirements such as sample type, desired resolution, and level of detail needed.

In here, SEM images of CNTs were taken between 3-7 kV and 2-3 spot size and as a conclusion, the most appropriate accelerating voltage and spot size combination for SEM analysis of CNTs among the examined parameters was found as accelerating of 3kV and spot size of 2.5 with more CNT surface information and details.

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