

## **Physicochemical Properties of Carbon Nanotubes (CNT's) Synthesized at Low Temperature using Simple Hydrothermal Method**

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### **Abstract**

Carbon nanotubes (CNT's) was successfully synthesis at low temperature using hydrothermal method. The reaction was carried out at 200°C for 24 hours using ferrocene and sulfur as carbon sources and catalyst, respectively which were mixed with 100 ml NaOH solutions (10 M). After hydrothermal treatment the product obtained was washed with ethanol and water until the washing solution is pH7. The solution was filtered and dried at 60°C for 24 hours to produce the CNT's. The synthesized CNT's was characterized using XRD, raman spectroscopy, SEM, TEM, and FTIR to study their physicochemical properties. XRD pattern shows the broad peaks assigned to graphite phase structure suggested that the synthesized sample was in carbon allotrope group. Raman spectra confirmed the presence of CNT's, with the observation of D and G bands at 1342 and 1592  $\text{cm}^{-1}$ , respectively. SEM result shows the produced CNT's had the diameter ~10 nm and several hundred nanometers in length with curly hair-like structures. Further investigation using TEM revealed the outer diameter of hollow elongated hair-like structures of CNT's are within 8 to 10 nm.

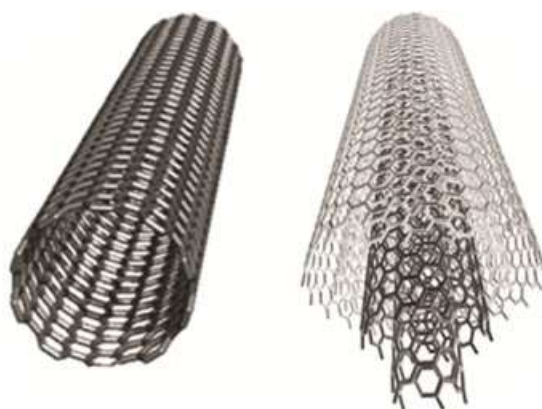
**Keywords:** nanomaterials, carbon nanotubes, low temperature, hydrothermal

### **INTRODUCTION**

Carbon nanotubes (CNT's) is a one dimensional (1-D) nanostructured materials made by rolling up a graphite sheet into tubular or cylindrical form [1]. They also can be described as a tube of carbon in nanoscale size. CNT's have variable diameters of few nanometers (approximately 1/50,000<sup>th</sup> of the width of a human hair), and their length

are up to several micrometers or millimeters. Each nanotubes is made up of a hexagonal network of covalently bonded carbon atoms. Chemical bonding of carbon nanotubes is completely in  $sp^2$  and this bonding structure is stronger than the  $sp^3$  bonds found in diamond. The  $sp$  bonding is one of the reasons of their superb strength. CNT's naturally align themselves into "ropes" held together by Van Der Waals forces [2]. However under high pressure situation, nanotubes can merge together, trading some  $sp^2$  bonds for  $sp^3$  bonds, giving the possibility of producing strong, unlimited-length wires through high-pressure nanotubes linking [3]. The strength of the  $sp^2$  carbon-carbon bonds gives carbon nanotubes amazing mechanical properties because they very strong along their axis, and also very flexible [4]. The Young's modulus of the best nanotubes can be as high as 1000 GPa which is approximately 5 times higher than steel. The tensile strength, or breaking strain of nanotubes can be up to 63 GPa, around 50 times higher than steel [5].

Generally, CNT's can be classified using several different methods, but the most common distinction made between nanotubes is by the number of walls in the tube. By this criteria nanotubes can be divided into two categories either single-walled carbon nanotubes (SWCNT's) consisting of a tube with a wall thickness of only one carbon atom, or multi-walled carbon nanotubes (MWCNT's) composed of many concentric tubes or shells. A SWCNT's is made by rolling one graphene sheet. When multiple graphene sheets are stacked upon each other and rolled into a cylinder with a common axis it will form MWCNT's. The structure of SWCNT's and MWCNT's can be seen in the Figure 1 [6].



**Figure 1:** Structure of single walled carbon nanotubes, SWCNT's (left) and multiwalled carbon nanotubes, MWCNT's (right)[6].

The synthesis of CNT's, either SWCNT's or MWCNT's, had been extensively developed since their discovery by Iijima in 1991 [7]. Among the well know methods were chemical vapor deposition, arc discharge and laser ablation. However, high temperatures (600-900°C), electric fields, evaporation, and vacuum are necessary conditions to prepare CNT's using these techniques. These conditions especially high temperature will contribute to high cost in synthesizing CNT's [8-10]. Latest technique

called hydrothermal synthesis method can produce CNT's at low temperature thus reduces the production cost of CNT in large scale. On top of that the hydrothermal synthesis of materials has many other advantages such as environmentally benign, simple and rapid. Hydrothermal method is the current ways that researcher develop in order to synthesize CNT's in large scale. Therefore this study uses hydrothermal method rather than others because of low temperature in synthesis process that will resulting in lower cost production of CNT's. CNT's have attracted great interest in multidisciplinary areas owing to their unique hollow tube structure and various potential applications.

## **MATERIALS AND METHODS**

### **Preparation of CNT's**

CNT's was prepared via simple hydrothermal method using ferrocene as a carbon precursor and sulphur as a catalyst respectively. 2 g of ferrocene and 4 g of sulphur was mixed with 100 ml of 10 M NaOH solution contained 70 ml ethanol and 30 ml distilled water under magnetic stirrer for 30 minutes. Next, the mixture was sonicated under an ultrasonic bath for 0.5 hours at ambient temperature and stirred again for 30 minutes. The resulting homogenous mixture was transferred into 200 ml teflon stainless steel autoclave reactor for hydrothermal treatment at 200 °C for 24 hours in electric oven. After the reaction was completed, the autoclave was cooled at room temperature naturally. The resulting black precipitate in autoclave was filtered and washed with ethanol and 0.1 HCl followed by distilled water until pH 7 of washing solution obtained. Then the black solid was separated and collected from solution and subsequently dried at 100 °C for 24 hours in an oven.

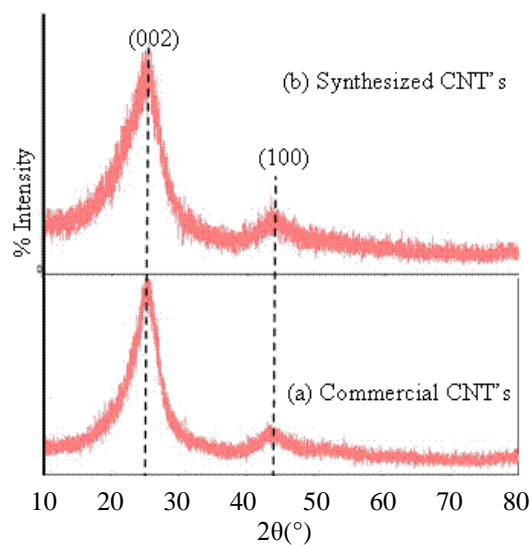
### **Characterization of CNT's**

X-Ray diffraction (XRD) analysis was performed using Bruker D8 Diffractometer with Cu-K $\alpha$  ( $\lambda=1.54021 \text{ \AA}$ ) and scans were performed in step of 0.2°/second over the range of 2 $\theta$  from 10 up to 80° for phase identification. Raman spectroscopy was carried out at room temperature using a Horiba Jobin-Yvon HR800 UV Raman spectrometer. The morphology of synthesized CNT's was studied using TEM and FESEM using ZEISS SUPRA<sup>TM</sup> 35VP FESEM and Philips CM12 TEM, respectively. FTIR analysis was conducted using Perkin Elmer FTIR Spectrum 100.

## **RESULTS AND DISCUSSION**

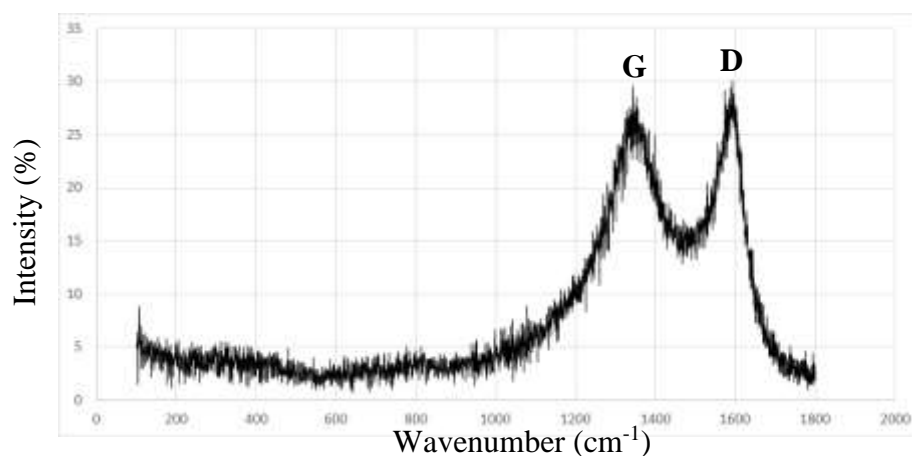
The XRD patterns of synthesized CNT as well as commercial CNT samples were depicted in Figure 2. Similar XRD patterns was observed for both samples in which two broad peaks were appeared at 2 $\theta$  25.07° and 43.19°, respectively attributed to the (002) and (100) planes of graphite [11]. Due to their intrinsic nature, the main features of CNT's XRD pattern is very close to those of graphite. Therefore, the X-ray diffraction profile cannot be used to differentiate microstructural details between the CNT's and the graphite structure. The structure of CNT's and graphite are very close to each other. They are formed by stacked graphene planes. Its unit cell is hexagonal

and contains four atoms [12].



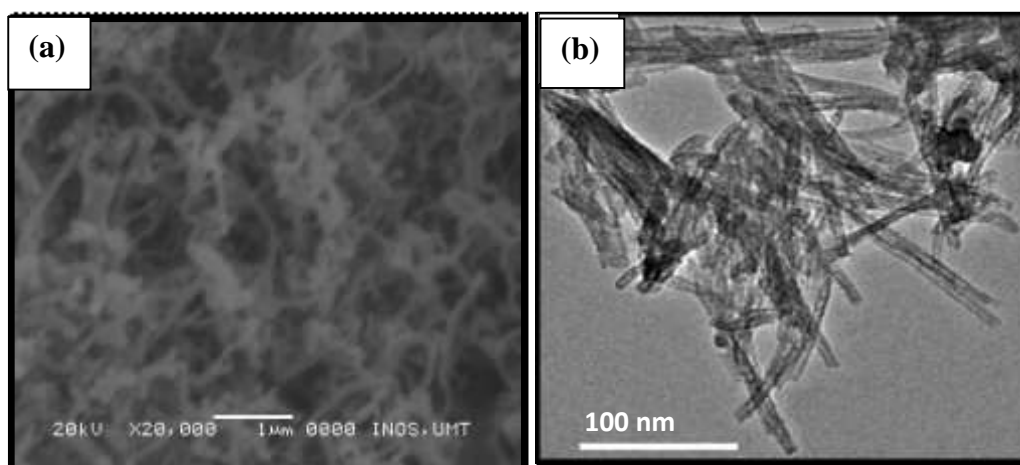
**Figure 2:** XRD pattern of the (a) commercial CNT's and (b) synthesized CNT's.

The synthesized CNT's was characterized further using Raman spectroscopy since it's an exceedingly powerful tool for CNT's characterization and classification. As shown in Figure 3, two broad peaks are observed at 1342 and 1592  $\text{cm}^{-1}$ , corresponding to the vibration of  $\text{sp}^2$  bonded carbon atoms in a 2D hexagonal lattice and the vibrations of carbon atom with dangling bonds in the plane terminations of turbostratic and poorly ordered carbon, respectively [13]. Most of the literature reported that peaks known as G (graphite) and D (disorder) bands. The shape of the G Raman peak gives possibility to distinguish between semiconducting or metallic nanotubes.



**Figure 3:** Raman spectrum of synthesized CNT's.

The morphology of the synthesized CNT was observed using SEM. As shown in Figure 4(a), large quantities of curly hair-like structure was observed. The diameter of the curly hair-like structure was determined to be 10 nm and up to several micrometers in length. The alignment of nanotubes is almost completely curve and wavy with no straight structure of carbon nanotubes. This might be due to the base-growth mechanism of CNT's, whereby the nanotube nucleates and grows above the catalyst.



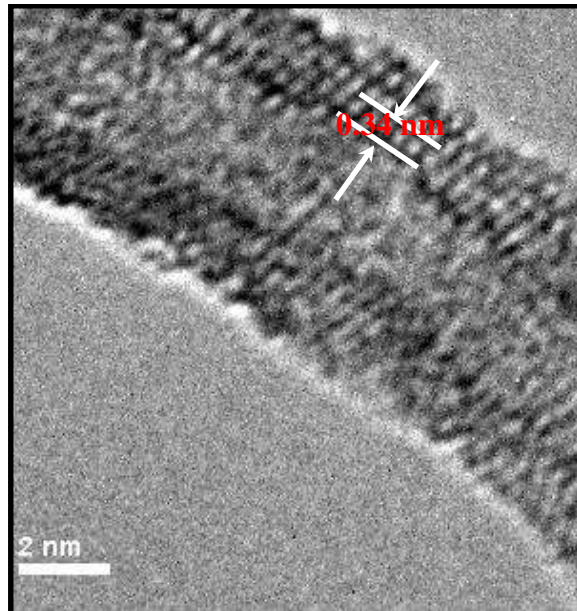
**Figure 4:** (a) SEM and (b) TEM micrographs of synthesized CNT's.

Further morphological structure of synthesized CNT's was investigated using TEM. The TEM micrograph in Figure 4(b) demonstrates the hollow elongated hair-like structure indicating nanotubes samples was obtained. The diameters of the nanotubes are within 8 to 10 nm. The CNT's normally show cylindrical morphologies with hollow channel along the full length. The lengths of the CNTs are from 200 nm to 1  $\mu\text{m}$  and the ratios of the length to the diameter are kept in the range of 20 to 30. The outer diameters and length of the nanotubes are slightly less than observed by SEM due to fractionation of CNT's during sonification before TEM analysis.

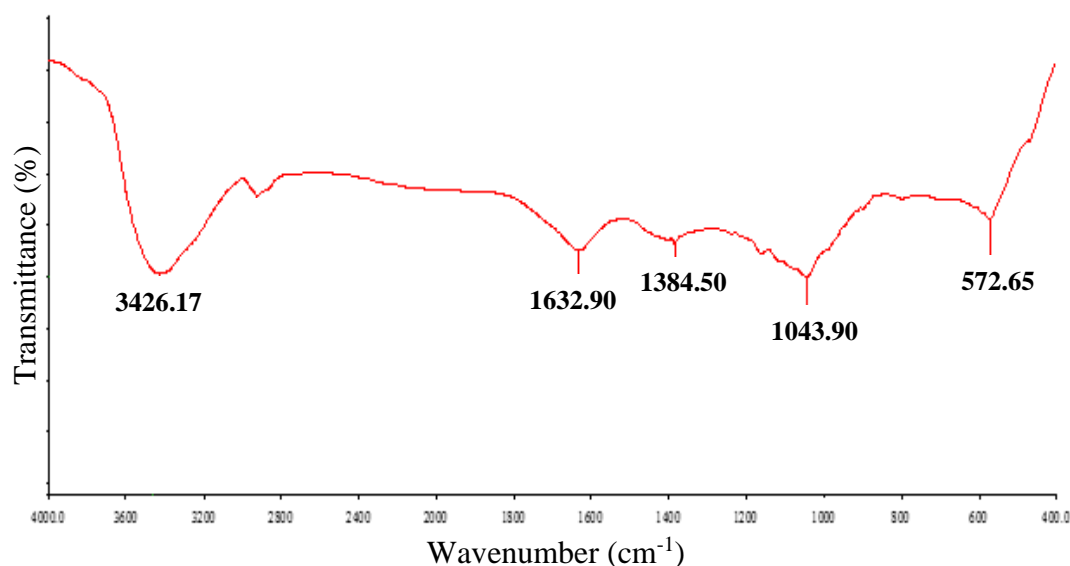
According to the HRTEM micrograph in Figure 5, the lattice fringes of the samples were clearly observed, which indicated the sample had high degrees of crystallinity [14]. The lattice fringes distance (d spacing) were determined to be about 0.3434 nm, corresponds to the (002) plane of carbon, indicating the product is comprised of the CNTs.

The formation of carbon nanotubes is predicted started with the reaction of ferrocene with sulphur to form ferrous sulphide and cyclopentadienyl group. Ferrous sulphide that formed will agglomerates into cluster and act as a catalyst where the carbon nanotubes were produced from the catalyst surface. According to Krishnamurthy and Namitha (2003), before carbon nanotubes was formed the ferrous sulphide catalyst reduces bis penta dienyl rings which is cyclopentadienyl group in high concentration of NaOH basic solution [15]. The usage of a high basic condition and an alcoholic environment are important in ensuring the formation of carbon nanotubes under hydrothermal condition. High concentration of NaOH also predicted to act as chemical

activation agent to activate carbon precursor to make it easily decompose into carbon elements and other products. The carbon with active surfaces is preferential for the growth of carbon nanotubes on the ferrous sulphide catalyst [16]. In order to remove the impurities, the grown CNT was washed with acid hydrochloric (HCl). This step is important and categorized as one of the chemical purification methods. This method is based on the idea of selective oxidation etching and the dissolution of metallic impurities by acids. The carbonaceous impurities are oxidized at a faster rate than CNT's therefore this step effectively removes amorphous carbon and metallic particles. This process also influences the structure of CNT's due to the oxidation involved where it often opens the end of CNT's, cuts CNT's, damage surface structure and introduces oxygenated functional groups ( $-\text{OH}$ ,  $-\text{C}=\text{O}$ , and  $-\text{COOH}$ ) on CNT's [17]. As can be seen in the FTIR spectrum of the synthesized CNT's in Figure 6, a broad peak at  $\sim 3426\text{ cm}^{-1}$  corresponded to the stretching vibration of the O-H functional group. This is due to the oxidation chemical purification process or probably from ambient atmospheric moisture. Another important peak due to the oxidation chemical purification is at  $\sim 1633\text{ cm}^{-1}$  and  $1384\text{ cm}^{-1}$  which is associated with the C=O and C-O bonds, respectively. Other bands in the fingerprint region ( $1100\text{--}500\text{ cm}^{-1}$ ) contain a complex set of absorptions, which are unique to each compound. Though these are hard to interpret visually, by comparing with references they allow the identification of specific compounds and most probably in this finding, it could be assigned to M-O (M-metal) bond representing the Fe-O stretching mode.



**Figure 5:** HRTEM micrograph of synthesized CNT's.



**Figure 6:** FTIR spectrum of synthesized CNT's.

## CONCLUSION

The CNT's have been successfully synthesized by hydrothermal method at low temperature (200°C). The formation of carbon nanotubes is predicted started with the reaction of ferrocene with sulphur to form ferrous sulphide. The ferrous sulphide act as catalyst where the CNT's were produced from the catalyst surface. The carbon (C) with active surfaces also is preferential for the growth of carbon nanotubes under hydrothermal condition. The synthesized CNT's are well crystallized and the diameter of nanotubes are within 10-12 nm with several hundred nanometers in length.

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