

Thermal and Electrical Properties of Carbon Nanotubes Purified by Acid Digestion

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Abstract—Carbon nanotubes (CNTs) possess unique structural, mechanical, thermal and electronic properties, and have been proposed to be used for applications in many fields. However, to reach the full potential of the CNTs, many problems still need to be solved, including the development of an easy and effective purification procedure, since synthesized CNTs contain impurities, such as amorphous carbon, carbon nanoparticles and metal particles. Different purification methods yield different CNT characteristics and may be suitable for the production of different types of CNTs. In this study, the effect of different purification chemicals on carbon nanotube quality was investigated. CNTs were firstly synthesized by chemical vapor deposition (CVD) of acetylene (C_2H_2) on a magnesium oxide (MgO) powder impregnated with an iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) solution. The synthesis parameters were selected as: the synthesis temperature of $800^\circ C$, the iron content in the precursor of 5% and the synthesis time of 30 min. The liquid phase oxidation method was applied for the purification of the synthesized CNT materials. Three different acid chemicals (HNO_3 , H_2SO_4 , and HCl) were used in the removal of the metal catalysts from the synthesized CNT material to investigate the possible effects of each acid solution to the purification step. Purification experiments were carried out at two different temperatures (75 and $120^\circ C$), two different acid concentrations (3 and 6 M) and for three different time intervals (6, 8 and 15 h). A 30% H_2O_2 : 3M HCl (1:1 v/v) solution was also used in the purification step to remove both the metal catalysts and the amorphous carbon. The purifications using this solution were performed at the temperature of $75^\circ C$ for 8 hours. Purification efficiencies at different conditions were evaluated by thermogravimetric analysis. Thermal and electrical properties of CNTs were also determined. It was found that the obtained electrical conductivity values for the carbon nanotubes were typical for organic semiconductor materials and thermal stabilities were changed depending on the purification chemicals.

Keywords—Carbon nanotubes, purification, acid digestion, thermal stability, electrical conductivity

I. INTRODUCTION

CARBON Carbon nanotubes with important structural and physical properties represent extraordinary opportunities for applications from energy storage to electronic nanodevices.

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An undesirable situation of many growth processes that CNTs contain residual growth catalyst and carbonaceous particles as impurities. Purification of these impurities without damaging the sample is really challenging procedure. Purification methods of CNTs can be basically classified into three categories, namely chemical, physical and a combination of both. The chemical method purifies CNTs based on the idea of selective oxidation, wherein carbonaceous impurities are oxidized at a faster rate than CNTs and the dissolution of metallic impurities by acids. This method can effectively remove amorphous carbon, polyhedral carbon and metal particles at the expense of losing a considerable amount of CNTs or destroying CNT structures. The physical method separates CNTs from impurities based on the differences in their physical size, aspect ratio, gravity and magnetic properties. In general, the physical method is used to remove graphitic sheets, carbon nanospheres, aggregates or separate CNTs with different diameter/length ratios. However, the physical method is always complicated, time-consuming and less effective. The third kind of purification is multi-step purification and combines the physical and chemical purification. This method can lead to high yield and high quality CNT products. Most importantly, one can selectively open tips, cut CNTs, add functional groups on sidewalls, separate CNTs according to length or conductivity or maintain an undamaged CNT structure by skillfully combining different techniques. The key point of this general method is how to combine different methods according to one's requirement and the quality of the raw CNTs [1]. Li et al. studied on thermal stability of carbon nanotube/silicone composites that changes via metal catalyst residues in carbon nanotubes [2]. They found that CNTs synthesized with cobalt catalysts decrease the thermal stability of silicone in CNT/SR composites, while CNTs synthesized with other metal catalysts did not show expected degradation. Sun et. al. [3] was found a simple and effective method for carbon nanotube dispersion in polymer matrix with dramatically increased electrical conductivity and thermal stability. They showed that the addition of multi-walled carbon nanotubes (MWCNTs) improve the thermal stability of their polymeric material and the electrical conductivities of the sPS/MWCNT composite was much higher than that of the neat sPS. Scheibe et. al. [4] studied on effect silanization procedures of oxidized and oxidized followed by sodium borohydride ($NaBH_4$) reduction of MWCNTs to obtain thermal and structural properties. They investigated the thermal stability of silanized MWCNTs samples in respect to the pristine MWCNTs. Yu et. al. [5] demonstrated a feasible approach to the preparation of multi walled carbon nanotube (MWNT)/polypyrrole (PPy) core–

shell nanowires by in situ inverse microemulsion. They were examined the thermal stability and electrical conductivity of the MWNT/PPy composites with thermogravimetric analysis and a conventional four-probe method. In comparison with pure PPy, the decomposition temperature of the MWNT/PPy (1 wt % MWNT) composites increased from 305 to 335 °C, and the electrical conductivity of the MWNT/PPy (1 wt % MWNT) composites increased by 1 order of magnitude. Zhang et al. [6] studied on a new method which was developed to disperse carbon nanotubes (CNTs) in a matrix polymer and then to prepare composites by melt processing technique and they investigated electrical conductivity and the rheological behavior of these composites and found that the conductive property was improved by increasing SWNTs. The conductivity of the composite containing 5 wt% SWNTs increases to 10^{-3} S/cm from that of 2.6 wt% SWNTs of 10^{-10} S/cm. In this study, thermal and electrical properties of single-walled carbon nanotubes (SWCNTs) purified by acid digestion was investigated. SWCNTs were firstly synthesized by chemical vapor deposition (CVD) method and purification process was fulfilled by different acids at different temperatures (75 and 120 °C) with different acid concentrations (3 and 6M) and for different time intervals (6, 8 and 15h). Nitric acid (HNO_3), sulphuric acid, hydrochloric acid and hydrogen peroxide were used in the removal of the impurities. The thermal properties of SWNTs were measured by thermogravimetric analyzer (TGA). Electrical properties were measured by electrometer. It was found that the obtained electrical conductivity values for the carbon nanotubes were typical for organic semiconductor materials and thermal stabilities were changed depending on the purification chemicals.

II. EXPERIMENTAL STUDY

A. Synthesis of Carbon Nanotubes

Carbon nanotubes were synthesized by the fluidized-bed CVD synthesis of acetylene (C_2H_2) on a magnesium oxide (MgO) powder impregnated with an iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) solution. The CVD apparatus consists of a vertical furnace and a quartz glass tube with a diameter of 3 cm in which in the middle a quartz filter (Fig. 1). A magnesium oxide ($100 \text{ m}^2 \cdot \text{g}^{-1}$) supported iron oxide powder produced by impregnation in an iron nitrate ethanol solution is used as precursor powder. To get a precursor with a MgO to Fe weight ratio of 5%, MgO were suspended in ethanol and iron nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) previously dissolved in 100 ml ethanol was stirred together and sonicated for 20 min in order to homogenize the mixture. Afterwards the precursor was dried and grinded into a fine powder. For one deposition, typically 0.75 g of precursor powder was filled in the quartz tube and the atmosphere was purged with argon for 5 min. Then the furnace was heated to the synthesis temperature (800 °C). By heating up the precursor powder iron oxide clusters were formed due to the thermal decomposition of the iron nitrate at 125 °C. The synthesis was started with the introduction acetylene mixed with argon for 45 min. After

synthesis, the CNTs were cooled in inert gas (argon). The total experimental time varied from 2 to 3 h with duration of actual growth stage 45 min.

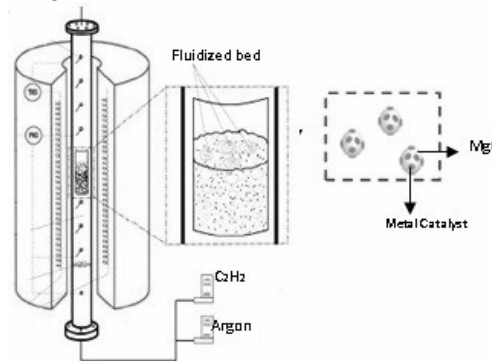


Fig. 1 Schema of the fluidized-bed reactor

A. Purification Procedure

The synthesized or as-grown samples were purified by applying acid digestion method to investigate the influence of purification on thermal and electrical properties of CNT material. Different chemicals (HNO_3 , H_2SO_4 , HCl and H_2O_2) with different concentrations (3M and 6M) for different times (6, 8 and 15h) at different temperatures (75 and 120 °C) were used in the removal of the metal catalysts from the synthesized CNT material to investigate the possible effects of each acid solution to the purification step. The purified samples were washed with distilled water until pH was reached to ~ 7 , and then dried in an oven at 105 °C for 48 h.

B. Characterization of Materials

The synthesized and purified CNTs were characterized by TEM-FEI Tecnai-G2 F-20 instrument, raman spectroscopy-Horiba Jobin-YVON HR 800UV instrument and thermogravimetric analyzer (TGA)-TA-Q600 SDT instrument.

C. Thermal Stability Measurement

The thermogravimetric analysis (TA- Q600 SDT model) was conducted to identify the thermal stability of CNTs. TG curves were obtained under air atmosphere at a heating rate of 10 °C/min from room temperature to 800 °C.

D. Electrical Conductivity Measurement

Electrical conductivity measurement of prepared samples was performed by electrometer of Keithley 6517A. The measurement was achieved at 20 °C temperature under 1 V electrical current. Thickness of samples was measured by digitally micrometer.

III. RESULTS AND DISCUSSION

A. Structure Characterization of CNTs

TEM image of the yield is given in Fig. 2. It has obviously seen from Fig. 2 that the structure which was synthesized by chemical vapor deposition method is CNT. Diameter of the

CNTs is nearly between 1.5-5 nm and also is so transparent. One possible explanation for the dark parts in figure is a result of the impurities within the structures. These observations lead to a conclusion: at the temperature of 800°C singlewall carbon nanotubes (SWNTs) were synthesized.

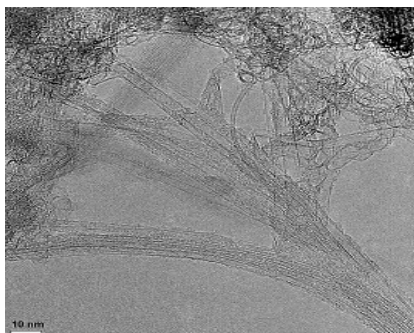


Fig. 2 TEM image of CNTs synthesized at 800 °C

Raman spectroscopy is a powerful technique for the characterization of the structure of carbon nanotubes. Fig. 3 shows Raman spectra for synthesized carbon deposit excited by 633 nm laser. Two different spectra of CNTs were observed at the G band (around 1580 cm^{-1}) and D band (around 1350 cm^{-1}). It is seen on Fig. 3 that the intensity of the G band is considerably higher than D band. The intensity ratio of D and G band (I_D/I_G) express the quality of CNTs. The higher ratio explains the higher amorphous carbon content and defect formation. The intensity ratio of G and D band of the synthesized CNT sample was found as 0.3125. This observation leads to a conclusion: CNTs have the low amorphous carbon content and defects. As seen from Fig. 3, the spectrum in RBM band, which is a characteristic of SWNT, was observed in the sample. The reason of this spectrum is that the tube diameter is below 2 nm and this result is consistent with other studies found in literature [7]. If nanotube diameter is greater than 2 nm, RBM spectrum becomes difficult to be observed.

RBM band has an another property that can be used to calculate the mean diameter of SWNTs by the equation (1);

$$\omega(\text{cm}^{-1}) = A / \text{dia}(\text{nm}) + B(\text{cm}^{-1}) \quad (1)$$

where; A and B are constants ($A = 223 \text{ cm}^{-1}/\text{nm}$, $B = 10 \text{ cm}^{-1}$) and d is the diameter of SWNT [8]. The calculated mean diameter of the synthesized SWNT sample was found as 0.94 nm.

Thermogravimetric (TG) analysis is used to characterize the total carbon loading and determine the residual metallic catalyst. The amorphous carbon is completely oxidized at temperatures below 350 °C and graphite burns above 750 °C.

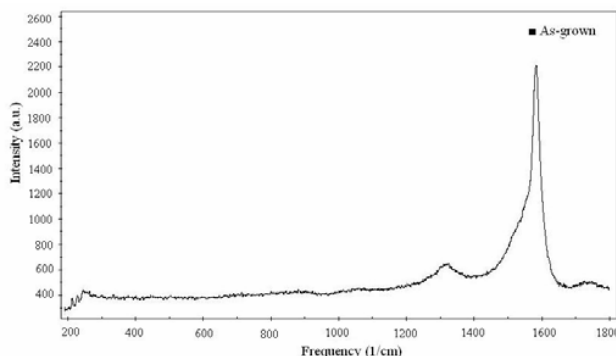


Fig. 3 Raman spectra of SWNT

The oxidation temperatures of the CNTs depend on the nanotube type and SWNTs is generally oxidized at the temperatures above 400 °C. In this study, the TG analysis of synthesized SWNTs was conducted in air atmosphere with a ramp of 5 °C/min between 25 and 800 °C. The yield was defined as the relative weight loss due to the oxidation of the carbon and the result of this analysis is shown in Fig. 4. As shown in this figure, carbon nanotube sample has high metal content (about 74%). Moreover, Derivative Thermogravimetric Analysis (DTG) of the sample was accomplished and the result is also shown in Fig. 4. Since the derivative curves directly reflect the variation in the weight as a function of temperature by occurrence of thermal events (such as the onset of burning), the discussion will focus on these. It can be seen that maximum weight loss of CNTs was occurred at 590°C (DTG_{max}). Especially, it is observed that DTG curve of the sample has only one peak which belongs to SWNTs. This is the also evidence of low amorphous carbon content of the sample. Similar situation is reported on the other studies in literature and oxidation of amorphous carbon below 400 °C is mentioned [9].

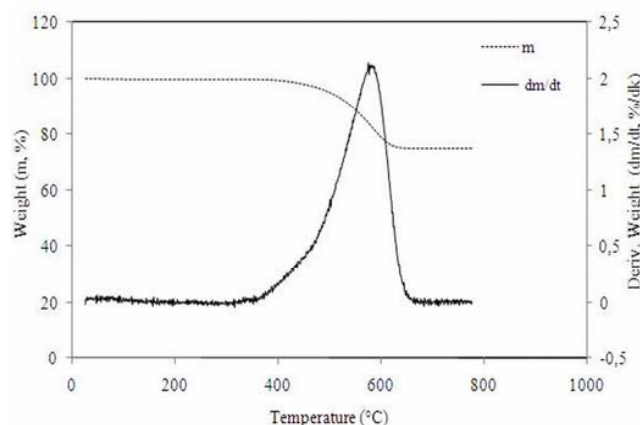


Fig. 4 TG ve DTG curves of SWNT synthesized at 800 °C

B. Purification of CNTs

In order to investigate the influence of product purity on thermal and electrical properties of SWNTs synthesized at 800°C were purified by different chemicals such as HNO_3 ,

H₂SO₄, HCl, HCl:H₂O₂ and HCl:H₂SO₄. TG analyses of the purified samples were performed in air atmosphere with a ramp of 10 °C/min between 25 and 800 °C. The results are shown in Table I. Purification yield was calculated according to the following equation (2):

$$\text{Purification yield (\%)} : (w_0 - w_t) / w_0 * 100 \quad (2)$$

where w_0 is the metal content of as-grown SWNT (%) and w_t is the metal content of purified SWNT (%).

Among the various acid purification treatments, TG analysis showed that HNO₃ was more effective in order to remove impurities (Table I). HNO₃ and H₂SO₄ removed metallic catalysts and oxidized carbonaceous impurities. Oxidized carbons called carboxyl, aldehyde, and other oxygen-containing groups [10] were formed up on SWNT sides. HCl was also effective chemical to remove metallic catalysts.

As a consequence, purification of SWNTs from its amorphous carbon and metallic impurities becomes more flexible during acid treatment.

TABLE I

THERMOGRAVIMETRIC ANALYSIS RESULTS OF THE PURIFIED SWNTs

Code	Concentration (M)	Acid	Time (h)	Temperature (°C)	Purification Yield (%)
1	3	HNO ₃	8	75	96.54
2	3	HCl	8	75	88.93
3	3	H ₂ SO ₄	8	75	91.24
4	3	HNO ₃	15	75	98.13
5	3	HCl	15	75	92.36
6	3	H ₂ SO ₄	15	75	94.44
7	6	HNO ₃	6	120	98.29
8	6	HCl	6	120	94.88
9	6	H ₂ SO ₄	6	120	97.70
10	6	H ₂ SO ₄ :HNO ₃	6	120	97.91
11	Concentrate:3M	H ₂ O ₂ :HCl	8	75	96.03
12	Concentrate:3M	H ₂ O ₂ :H ₂ SO ₄	8	75	94.67

TG curves of SWNTs that were purified by different chemicals are shown in Fig. 5. The lines reflected the weight loss upon heating and their shape were dependent on the composition and the oxidative stability of the sample components. A final temperature of 800 °C was sufficient for complete burning of the nanotubes and carbon impurities such as graphite and amorphous carbon that were completely burned at the temperatures of 625-660 °C. The residual weights (%) after the heating process showed the presence of metallic impurities. The sample purified by 6M HNO₃ for 6h at 120°C had 1.27% residual weight belonging to catalyst particles. While the sample purified by 3M HNO₃ for 8 h at 75°C demonstrated a residual weight of nearly 2.57%, at the conditions for 15h the residual weight of sample is 1.39 % which suggested more efficient removal of metallic catalyst. When the sample purified by 3M H₂SO₄ and 3M HCl at 75°C are analysed the residual weights are found 6.49% and 8.21% for 8 h and 4.12% and 5.66% for 15h, respectively. The

sample purified by 6M H₂SO₄, 6M HCl and 6M H₂SO₄:HNO₃ for 6h at 120°C showed residual weights about 1.70 %, 3.79% and 1.55%, respectively. These results indicated that HCl, treatments were not as effective as other acids for the removal of all catalyst. To remove both metal catalyst and amorphous carbon, the sample purified by H₂O₂:HCl and H₂O₂:H₂SO₄ at 75°C for 8h had 2.94% and 3.95% the residual weights.

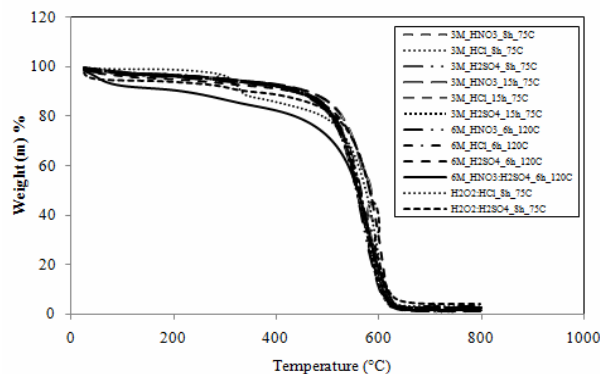


Fig. 5 TGA curves of SWNTs purified by different chemicals

DTG analysis of the samples was also accomplished and the results are shown in Fig. 6. DTG curves consist of broad peaks in different positions, suggesting an influence of the purification treatments on the thermal stability. When the DTG curves of purified samples are analyzed it can be seen that the sample purified by 6M HNO₃ for 6h at 120°C has two different peaks. First one can be explained with defect formation that is result of SWNT damage during the acid treatment. Second peak belongs to single wall carbon nanotubes. According to the DTG curves, T_i (the initial degradation temperature) and T_p (peak temperature which corresponds to the maximum weight loss of the sample) values of purified samples are given in Table III.

TABLE III

THERMAL PROPERTIES OF SINGLEWALL CARBON NANOTUBES PURIFIED BY ACID DIGESTION

Code	T_i	T_p
1	463.18	573.37
2	508.47	599.29
3	577.19	584.77
4	580.03	630.27
5	508.47	599.29
6	582.07	633.25
7	443.89	637.63
8	483.32	586.41
9	506.09	606.57
10	467.23	579.08
11	504.86	595.87
12	593.44	628.51

T_i and T_p values or maximum weight losses changed depending on the purification efficiency. T_i values of the purified SWCNTs were higher than as grown SWCNT (430°C). The maximum weight losses of SWNTs purified by 3M HNO₃ and 3M H₂SO₄ for 15h at 75°C were occurred at 578 °C while it was at 588 °C for the SWNT sample purified

by 3M HCl at the same conditions. These values were higher than samples purified by 3M HNO₃, 3M H₂SO₄ and 3M HCl at 75°C for 8h which have the maximum weight losses at 560°C and 583°C. The maximum weight losses of SWNTs purified by 6M HNO₃, 6M HCl and 6M H₂SO₄ for 6h at 120°C were taken place at 495 °C, 575°C and 593°C, respectively while it was 565 °C for the SWNT sample purified by 6M H₂SO₄: HNO₃ at the same conditions. The sample purified by H₂O₂: HCl represented different behavior by showing two peaks at the temperatures of 318 and 586 °C. The first peak could be explained according to Fenton process that iron hydroxyl complex were removed at this temperature. Second peak is attributed to the oxidation of the carbon nanotubes. DTG curves clearly demonstrate that oxidation temperatures of the purified samples are lower than that of the as-grown sample. Comparison of the purified samples represents that the oxidation temperatures of the samples purified by HNO₃ and H₂SO₄ are much lower than the others.

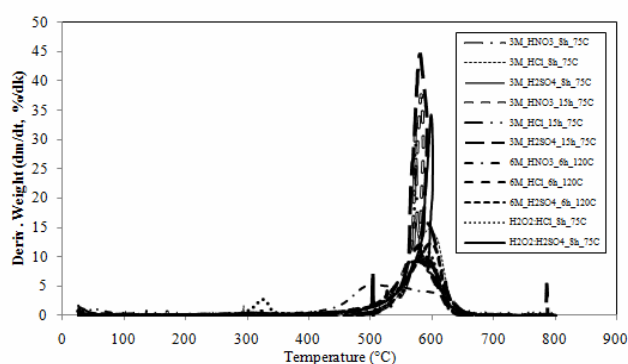


Fig. 6 DTG curves of SWNTs purified by different chemicals

Raman spectra of the samples purified by different chemicals (Fig. 7) observed the strong peaks at nearly 1590 cm⁻¹ on G band were attributed to typical peak of SWNTs. The peaks at around 1300 cm⁻¹ on D band indicates the presence of amorphous carbon. Because D band indicates disordered sp² hybridized carbon atoms and G band reflects the structural integrity of the sp² hybridized carbon atoms of the nanotubes. I_D/I_G ratio correlates with nanotube quality and the decrease in the amount of the amorphous carbon in graphitic materials in the sample. When the I_D/I_G ratios of samples (Table II) were compared, it's seen that the sample purified by 3M HNO₃ for 15h at 75°C and 6M H₂SO₄:HNO₃ for 6h at 120°C were highly damaged after purification.

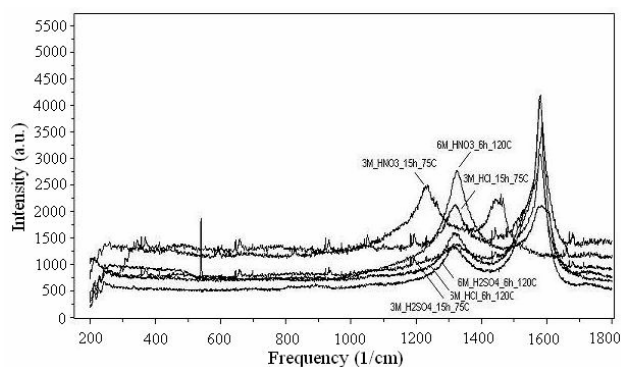


Fig. 7 Raman spectra of SWNTs purified by different chemicals

The mean diameters of the purified CNT samples were also calculated according to equation 1 and the calculated diameters of CNTs are shown in Table II. When the diameters of the purified samples were compared with as-grown sample, there was a little decrease on diameters of samples purified by H₂SO₄ and HNO₃. The sample purified by H₂O₂:HCl had nearly the same diameter.

TABLE II
THE MEAN DIAMETER AND THE INTENSITY RATIO OF D AND G BAND OF THE PURIFIED SAMPLES

Code	Diameter (nm)	I _D /I _G
4	0.85	1.06
5	1.03	0.59
6	0.60	0.45
7	0.93	0.66
8	1.03	0.37
9	0.96	0.32
10	1.12	1.33
11	1.07	0.63

Electrical conductivity measurement of purified samples was performed by electrometer of Keithley 6517A. The measurement was achieved at 20°C temperature under 1 V electrical current. Thickness of samples was measured by digitally micrometer and the results are given in Table IV. The results showed that purification conditions such as acid concentration, time and temperature affect on the electrical properties of SWCNTs. As seen in Table IV, when the concentration, time and temperature change for HNO₃ treatments electrical conductivities were measured 59.2, 86.27 and 124.79 S/cm. These values show that when the purification efficiency of the SWCNTs increases the electrical conductivity values also increase. The same situation was observed for H₂SO₄. The electrical conductivity of sample purified by H₂O₂:HCl which is effective to remove both metallic impurities and amorphous carbon was found as 90.08 S/cm. These observations lead to a conclusion: the electrical conductivity values for the purified SWCNTs were typical for organic semiconductor materials.

TABLE IV
ELECTRICAL CONDUCTIVITY OF SINGLEWALL CARBON NANOTUBES PURIFIED
BY ACID DIGESTION

Code	σ (S/cm)
1	59.42
2	69.09
3	38.09
4	86.27
5	32.63
6	42.55
7	124.79
8	124.26
9	90.71
10	37.35
11	90.08

IV. CONCLUSION

This study indicates that the thermal stability and electrical conductivity of carbon nanotubes which were synthesized by chemical vapor deposition method and purified by different chemicals change according to purification conditions. It was determined that the thermal stability of SWCNTs increase depending on the purification efficiency. Furthermore, the electrical conductivity values of the synthesized and purified samples changed within the range of 37.35 to 124.79 S/cm. It was concluded that the electrical conductivity values for the purified SWCNTs were typical for organic semiconductor materials.

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