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Experimental Study On The Purification Of Carbon Nanotubes Using Carbon Dioxide Gas As An Oxidation Reagent

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Abstract : *The fabrication and application of carbon nanotubes (CNTs) have been strongly investigated and developed recently. However, the application of CNTs usually encounters a great limitation that the unique properties of CNTs will be reduced by impurities such as metal catalyst particles and amorphous carbon after synthesizing. Therefore, in this study, we focus on the purification method for CNTs using CO_2 as a gas phase oxidation reagent to remove the amorphous carbon content. Morphology and structure of CNTs were then evaluated by SEM, TGA, Raman, showed that the purity of CNTs increased up to 98%, which could be used to develop the application research of this advanced material.*
Keywords-*Carbon nanotubes, amorphous carbon, purification, structure*

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I. INTRODUCTION

Since discovered by Sumio Iijima in 1991, CNTs have gained intensive attention due to their unique physical and chemical properties. With the belief that CNTs will be a key to resolve outstanding issues of modern technology, CNTs have been applied to numerous scientific fields such as physics, chemistry, biology, and electronic devices. Recently, a number of groups succeeded in fabricating CNTs by various methods including arc discharge, laser ablation, and chemical vapor deposition (CVD). Unfortunately, impurities existing in the production of the above method such as amorphous carbon, fullerene spheres, and metal particles have a negative influence on the properties of CNTs. Because high-tech applications require cleanliness of CNTs, it is necessary to purify of fabricated CNTs. Compared to CNTs, carbon impurities are more susceptible to oxidation due to there are a much more feeble connection and defects in the structure. To remove amorphous carbon from CNTs, the methods of gas phase oxidation using air, O_2, Cl_2, H_2O, CO_2 or liquid phase oxidation using acids can be employed. However, the disadvantage of liquid phase oxidation is that the structure of CNTs could be altered. Being cut into shorter tubes or functionalized with carboxyl and hydroxyl groups weaken the excellent properties of CNTs significantly.

To purify of fabricated CNTs, there are various methods divided into three groups: chemical methods, physical methods, and chemical-physical combined methods. Purification of CNTs using chemical methods is based on oxidation of carbon (the oxidation temperature of amorphous carbon is lower than CNT) and metal dissolution with acid. Therefore, this method can remove the amorphous carbon and metal particles from CNTs. Chemical methods, however, often cause defects in the structure of CNT materials due to the oxidation. Physical methods are developed based on differences in the size, weight, magnetic properties of the components in the fabricated CNTs. However, compared to chemical methods, the physical method is complex, time-consuming and inefficient. The third method is the combination of the chemical method and the physical method showing as a promising method for of purification of CNTs.

In this paper, we present the results of the study on removing the amorphous carbon content by using CO_2 as a gas phase oxidation reagent to purify CNTs fabricated by the CVD.

II. EXPERIMENTAL

Multi-walled carbon nanotubes (MWCNTs) were produced by a chemical vapor deposition (CVD) process using $Fe/CaCO_3$ as catalytic material [11]. As synthesized MWCNTs were purified using a flowchart as shown in Fig. 1. Firstly, MWCNTs were treated by HCl acid (36.5%) for 24 hours to remove remained catalytic such as Fe and CaCO3, then filtered thoroughly with distilled water and dried to obtain MWCNTs powder. Secondly, gas oxidation using CO_2 was applied to remove the amorphous carbon content. HCl purified MWCNTs were added to the incubation furnace and treat at varying temperatures of 600^{o}C, 650^{o}C, and 700^{o}C.

Oxidation time was investigated with different time intervals of 30 minutes, 60 minutes, 90 minutes and 120 minutes. the CO2 flow rate was fixed to be 200 sccm.
The morphology of the CNTs after cleaning was evaluated by scanning electron microscopy (SEM) method on the FESEM Hitachi S4800. The purity of CNTs was evaluated using Thermo-gravimetric analysis (TGA) and the structure was investigated by Raman scattering.

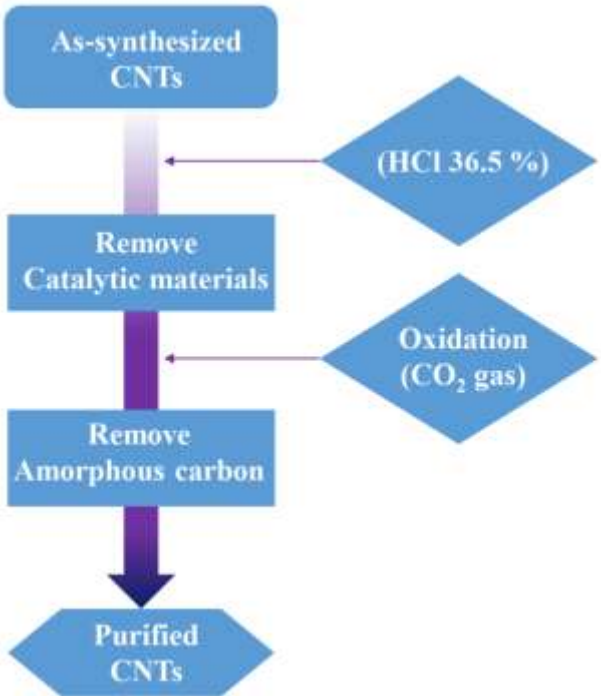

Fig. 1: Purification process for carbon nanotubes

III. RESULTS AND DISCUSION

Fig. 2 shows SEM images of MWCNTs purified by HCl solution and gas oxidation at different temperatures. Some amorphous carbon remained after cleaning by HCl as shown in Fig. 2a. This indicated that is difficult to be removed the amorphous carbon content by HCl solution. After using CO_2 oxidation at 600^{o}C, the major part of amorphous carbon were removed and the diameter of CNTs was determined in the range from 50 to 100 nm. Fig. 2c shows the SEM image of the CNTs oxidated at 650^{o}C in CO_2 for 90 min. As observed, there are no amorphous carbonaceous materials, the tube is very straight, no debris appears on the tube wall. It means that the purity of MWCNTs was much improved. However, as increasing the oxidation temperature up to 700^{o}C, having some re-occurrence of impurities. This is attributed to the partial burning of carbon nanotube occurred. Based on the SEM analysis, it is found that the optimum oxidation temperature for removing the amorphous carbon content is determined to be 650°C.

To evaluate the effect of oxidation temperatures and oxidation time on the mass loss of MWCNT, we conducted the study at different temperatures of 600°C, 650^{o}C and 700°C (Fig. 3). The obtained results indicated that if the oxidation temperature is 700^{o}C or higher, the weight loss is very high about 40 to 50%. The reason for this is due to the burning not only the amorphous carbon but also a part of CNTs. Therefore, to maintain the structure of CNTs during the oxidation process the oxidation temperature below 700oC is recommended.

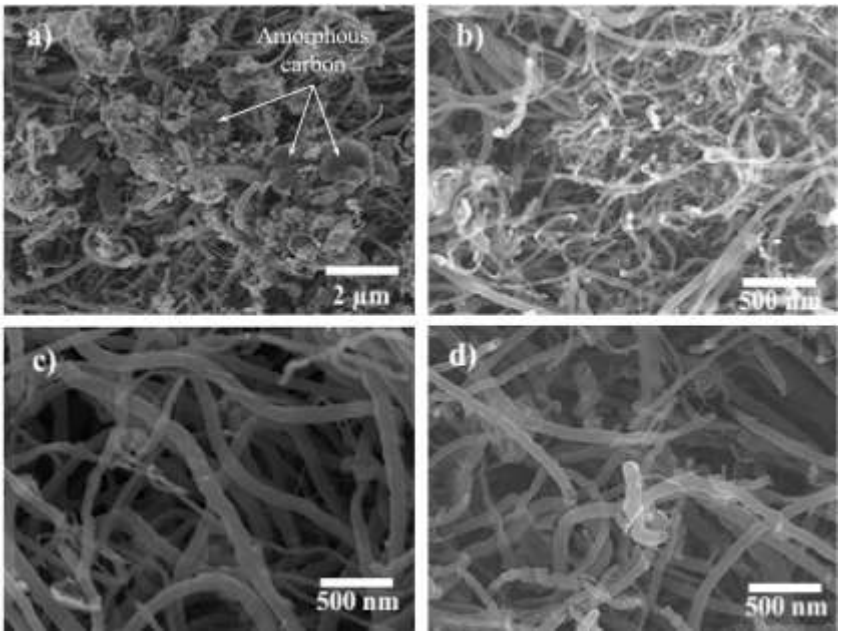

Fig 2.SEM images of MWCNTs purified by HCl solution (a) and combinated gas oxidation at different temperature of 600^0C (b), 650^0C (c), 700^0C(d).

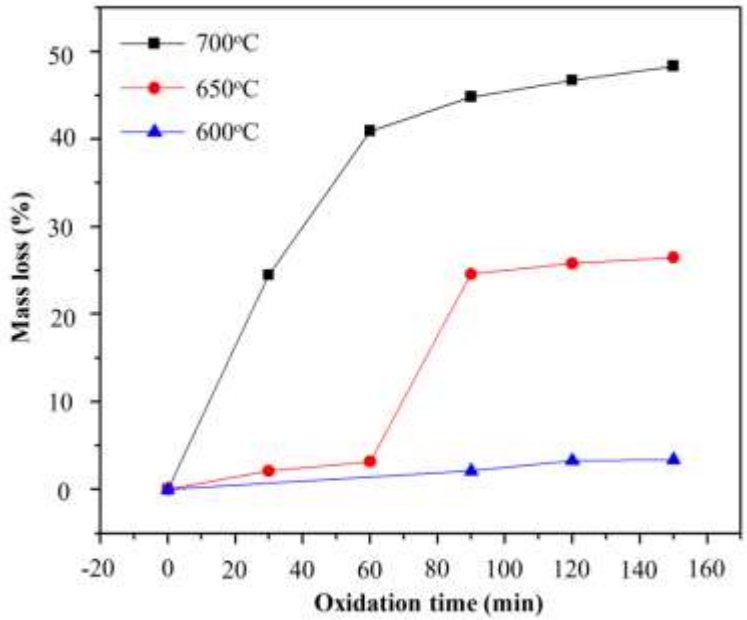

Fig. 3. Mass loss of MWCNTs as a function of oxidation time

For further evaluation we used TGA (thermal analysis), this is the analysis of the temperature of the combustible material in the environment. The amorphous carbon fraction is usually decomposed in air at lower temperatures for MWCNTs. The TGA method is used to examine the results. Figure 4 shows (a) TGA and (b) DTGA curves of the MWCNTs purified by HCl solution and CO_2 oxidation at a temperature of 650^oC for 90 minutes. As shown in Fig 4, the HCl purified MWCNTs begins to burn at a temperature of 407^oC and the line attenuation starts from the highest temperature and attenuation at 578^oC expressed on the DTGA curve. We found that the TGA curve of the sample did not clean strongly and decreased rapidly to $578^oC \div 582^oC$ at a loss of 90% and then decreased to 697^oC and the loss was 92%. As for the TGA curve of purified MWCNTs with CO_2 oxidation, the curve is smooth and prolongs to 697^oC and ends with about 98% weight loss. This demonstrated that the amorphous carbon component was removed and additionally removed other impurities. As a result, the purity of MWCNTs was improved from 90% to 98% by a combination of chemical and gas oxidation treatment.

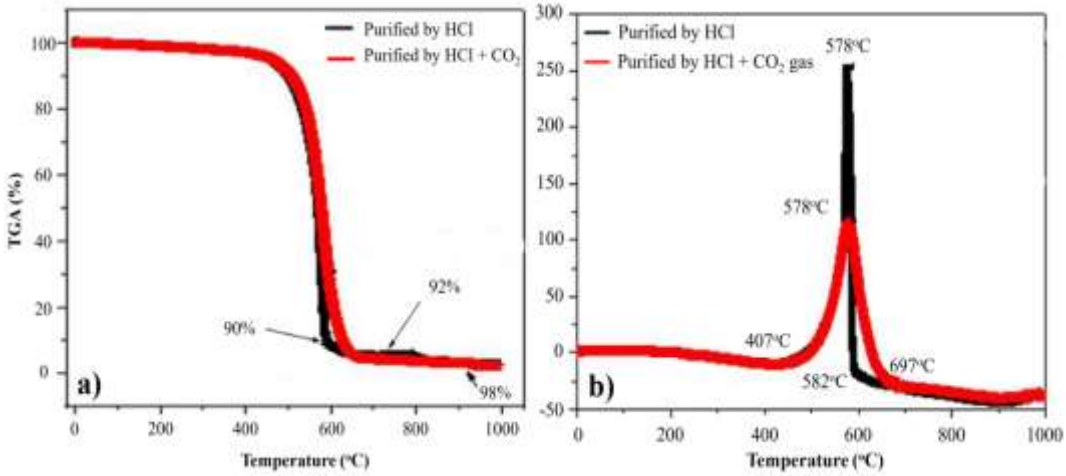

Fig.4: a)TGA and DTGA curves of MWCNTs purified by HCl solution and gas oxidation

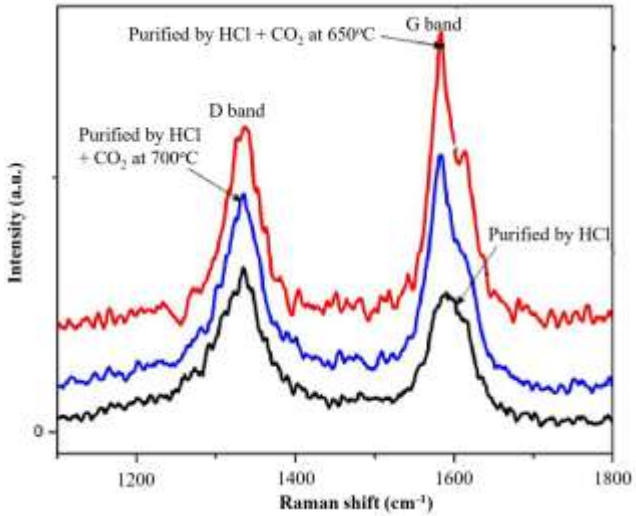

Fig. 5: Raman spectra of MWCNTs purified by HCl solution and gas oxidation at different temperature of 650^{o}C and 700^{o}C.

To evaluate the structural defects of MWCNTs before and after purification, we used a non-destructive analysis of material structure called Raman spectral scattering. Figure 5 shows the Raman spectra of MWCNTs were purified by HCl solution and plus gas oxidation at 650^{o}C and 700^{o}C. The Raman spectra results show that there are two main bands, the D band and the G band. The D band corresponds to the wave number of ~ 1333 cm $^{-1}$ corresponding to the irregular structure and the defect in the structure of the graphite including sp^3 hybrid state. G band (~ 1583 cm^{-1}) corresponds to the ordered state of carbon in the graphite network. In order to assess the cleanliness of MWCNTs in Raman scattering we need to determine the relative intensity ratio of D band and G band (I_D/I_G). This ratio depends on the purity and structure of the material. The intensity ratio of I_G/I_D ratio was determined to be 1.18, 0.89 and 0.69 for MWCNTs purified by only HCl solution and combination HCl and CO_2 oxidation at 650^{o}C and 700^{o}C, respectively.. It was found that the sample after oxidation treatment was better than the untreated sample, and the CNTs treated at 650^{o}C showed a better purify than the sample at 700^{o}C due to less defect. The results are very consistent with the results of SEM and TGA analyzes.

IV. CONCLUSION

We have investigated the purification method for MWCNTs synthesized by CVD method. The combination of the chemical method using HCl acid solution (36.5%) and gas oxidation process in CO_2 demonstrated as a promising method in removing the impurities such as metal catalyst, CaO, and amorphous carbon. The best condition for the gas oxidation process is at 650^{o}C for 90 min. The proposed purification process possible to eliminate about 5% to 10% amorphous carbon and the purify of MWCNTs obtained up to 98%. The obtained high-purified MWCNTs are suitable for high-tech applications such as composite, electronic, etc.

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