

Harmonized processing of biomorphic materials for the synthesis of carbon nanotubes

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A three-step process was carried out to form carbon nanotubes (CNTs) on a biomorphic carbon template (BCT). First, natural wood with 20- μm pores was transformed into a carbon template via carbonization pyrolysis. Thereafter, LTA zeolite crystals were synthesized to have a crystal size of 0.3 μm , and an *in situ* hydrothermal process was used to coat the BCT with a single, homogeneous zeolite layer. Finally, CNTs were synthesized on the zeolite-coated biomorphic carbon template (ZCBCT) via catalytic chemical vapor deposition (CCVD) with acetylene (C_2H_2) as a carbon source. In this study, we focused on varying the reaction time and temperature to improve the CNT yield and assess the morphology, crystallinity, and yield percentage of the CNTs. Multi-walled CNTs with an inner diameter of 10.7 nm were synthesized at 650 °C, and a maximum CNT yield of 7.09% was obtained at 180 min.

Key words: Carbon nanotubes, Biomorphic carbon template, Carbonization, Hydrothermal, Catalytic chemical vapor deposition.

Introduction

Since the discovery of carbon nanotubes (CNTs) by Iijima et al. in 1991, many researchers are attracted due to its unique morphological, physical and chemical properties [1, 2]. CNTs research reported applications in numerous fields, such as electronics, electromagnetic devices [3], composite materials [4], optical devices, biomedical materials recently energy storage [5, 6] and filter applications [7].

As their applications are related to the quality of CNTs thus produced, the synthetic method has been improved several times by the time of its discovery, which includes electric-arc-discharge, laser ablation and chemical vapor deposition (CVD) [8-10]. Especially, the catalytic chemical vapor deposition (CCVD) has been proved to be more efficient synthetic method due to its simple operating condition, low-cost, high yield and quality production ability [11]. In fact, the synthesis of CNTs from the decomposition of carbon-containing gas over the metal particular catalysis (Co, Fe, Ni, Cu or their binary mixtures, related oxides) surface has been researched for a long time [12].

However, with their size decreasing to the nanoscale, metal particles have a strong agglomeration tendency during the synthesis of CNTs. Therefore, maintain the morphology and size of these particles at CVD

processing temperature (650-750 °C) is essential to template coated porous ceramics and also nanostructured biomorphic carbon materials to homogeneously penetrate carbon source (e.g. CH_4 , C_2H_2 etc.) [13, 14]. In general, catalyst supports or matrices, such as alumina [15], mesoporous silica [16], and zeolite [17], have been used to prevent the agglomeration of catalyst nanoparticles. Among them, zeolites are considered excellent template for supporting or encapsulating the catalyst nanoparticles because of their well-defined pore structures and high surface areas [18], thereby leading to catalyst particle stabilization, producing a fine dispersion of nanoparticles, and increasing the number of nucleation sites which is advantageous to the high yield synthesis of CNTs [19-20].

The biological bulk materials with unique and sophisticated structures can be obtained from the natural evolution through ages [21]. Upon carbonization of wood such as cypress (Hinoki), red pine and picea (Gorman spruce) etc., biomorphic template is produced, which contains a considerable amount of pores, which act as an effective base for the growth of carbon nanotubes (CNTs) at higher temperatures. This gives an alternative to the use of transition metal catalysts which are commonly used for the synthesis of CNTs [22].

In this study, the formation of CNTs in zeolites coated biomorphic carbon template by CCVD method is reported. The synthesis was carried out with the application of the three different processing routes for CNTs composites. First of all, biomorphic carbon template (BCT) was produced by the carbonizing reaction.

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Secondly, LTA zeolites were synthesized within and coated simultaneously on the carbon template, which was then subjected to colloidal process resulting in the formation of Co ions-supported zeolites-coated carbon template and finally, CNTs were synthesized by CCVD method was used for the synthesis of CNTs. The effects of reaction temperature and time on the morphology and yield of CNTs were investigated. Thus, the synthesized CNTs-carbon matrix was analyzed for microstructural properties, morphology and the yield percentage by HRTEM, FESEM, TGA and Raman spectra.

Experimental

Raw materials

Natural wood Spruce (*Picea*, Gorman Bros. Lumber Ltd., Canada) was carbonized to form a honeycomb porous carbon template. Aluminum isopropoxide (AIP, 98+%), Tetraethyl orthosilicate (TEOS, 98%), Tetramethylammonium hydroxide (TMAOH, 25% hydroxide solution), and Sodium hydroxide pellets (NaOH, 99.998%), were purchased from Sigma-Aldrich, and were used to synthesise LTA zeolite crystal. Cobalt chloride hexahydrate ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O} \geq 99.0\%$, Samchun Chemical) was taken as the catalyst, and acetylene (C_2H_2 , Kyuonin Chemical Industry) was used as the carbon source. Further chemicals used Nitrogen (N_2 , 99.99%, Doekyang Co. Ltd), de-ionized water and Ethanol (EtOH, 94.5%, Samchun Chemicals).

Preparation of biomorphic carbon template:

BCT are prepared in two steps. Primarily a carbon template was prepared by the pyrolysis of spruce specimens in presence of inert gas to maintain neutrality. To avoid the collapse of the sample during the carbonizing process, the samples were gently heated up to 600 °C with a heating rate of 0.5 °C/min for 6-8 hrs in a horizontal electric furnace with N_2 gas flow (10 sccm). Subsequently, the temperature was raised up to 1,000 °C at the rate of 3 °C/min to get accrue a porous carbon template. Fig. 1(a) shows that during the pyrolysis, H_2O , carbonyl groups and alcohols are released by the decomposition of

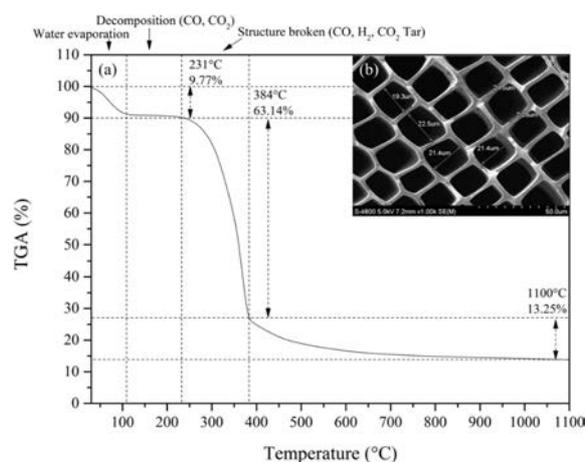


Fig. 1. TGA curves and FE-SEM image of carbonized biomorphic carbon template (Spruce).

biopolymer structures at temperatures up to 600 °C. Meanwhile, the major biopolymer constituents of cell wall materials are rearranged and converted into carbon struts. Under pyrolysis at the initial stage ($T \leq 250$ °C), the evaporation of water and decomposition of oxocarbon starts with the weight loss of 20%, and then the structure of wood breaks (CO , H_2 , CO_2), and changes into charcoal having 30% tar between 300 and 500 °C with the weight loss of 80%. Fig. 1(b) shows that the unique structural features of the original tissue can be retained during pyrolysis, which yields a porous template with honeycomb carbon structure.

Zeolites synthesis, coating and catalyst loading

To synthesize the LTA zeolites, a mother solution with a molar ratio of $\text{Al}(\text{i-pro})_3 : \text{TEOS} : \text{TMAOH} : \text{NaOH} : \text{H}_2\text{O}$ of 1 : 2.2 : 2.4 : 0.3 : 200 was prepared, and stirred for 8-12 hrs. The carbon template was dipped into the zeolite mother solution, and allowed to age for 12 hrs. Afterward, the carbon template in a zeolite mother solution was moved into a Teflon-lined stainless steel pressure vessel and was hydrothermally treated at 90 °C for 3 days, as shown in Fig. 2(b). The zeolite-coated biomorphic carbon templates (ZCBCT) were dispersed by colloidal processing of an aqueous CoCl_2 solution (metal content ~ 0.8 mmol). In this

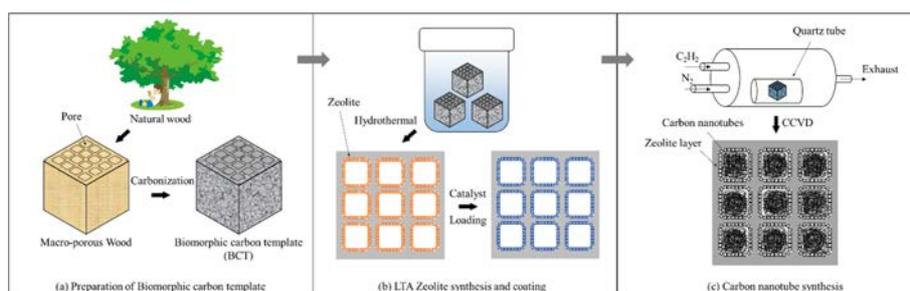


Fig. 2. Schematic diagram of growing Carbon nanotubes on BCT: (a) Preparation of biomorphic carbon template, (b) LTA zeolite coating, and (c) Carbon nanotube synthesis.

process, the Co ions from aqueous CoCl_2 solution were supported on the template. This template was dried overnight at room temperature and calcined in an electric tube furnace at 450°C for 4 hrs in N_2 atmosphere. The Co-supported zeolite-BCT was designated as CZBCT.

CNTs synthesis

Fig. 2(c) shows the schematic figures to show the process of the synthesis of CNTs in a CZBCT. The catalytic decomposition of carbon source (acetylene) on the carbonized carbon template was carried out in a quartz tube centered in an electric tube furnace. The temperature was raised a rate of $5^\circ\text{C}/\text{min}$ to the desired reaction temperature in a nitrogen atmosphere (200 sccm) to maintain neutrality. Carbon nanotubes were grown by the introduction of carbon feeding gas C_2H_2 (10 sccm). CNTs were separately synthesized at 650°C and 700°C for 40, 60, 120, and 180 min, respectively.

Results and Discussions

Fig. 3(a), (a') and (a'') shows the ZCBCT with different magnification obtained displays a square shape cell structure with $19.3 \sim 22.5 \mu\text{m}$ range pore size (in length), and around $2.45 \mu\text{m}$ thick cell wall. The LTA zeolites are finely coated inside of honeycomb structure which can be observed in Fig. 3(a''). As shown in Fig. 3(b), the horizontal view of ZCBCT can be observed. The cubic shape of LTA zeolite crystals has been achieved with the size of around 120 nm. The cube $\{001\}$ is composed of six perfect square faces that make angles of approximately 90° . The crystal structure of LTA zeolites was homogeneously synthesized and coated on the surface of the template by an *in situ* hydrothermal process. Generally, the framework of LTA zeolite crystals can be explained in terms of two types of polyhedral; one is a simple cubic alignment of eight tetrahedral, and is termed D4R; and the other is a truncated octahedron of

24 tetrahedral or cages, as previously described for the sodalite-type minerals [18]. The LTA zeolite is generated by placing the cubic D4R units in the center of the edges of a cube with an experimental lattice constant of 12.389 \AA as shown in Fig. 3(b''). The XRD pattern of synthesized LTA zeolite and the diffraction peaks of coated sample correspond with JCPDs card No. 39-0223, which is a single phase of LTA zeolite is shown in Fig. 3(c).

Fig. 4 shows FE-SEM images of CNTs that are synthesized on CZBCT by the CCVD method. Each image represents synthesis at 650°C for 40, 60, 120 and 180 min., respectively. All the images clearly show CNTs synthesized inside and around pores. In particular, CNTs grew intensively over the cell wall. Fig. 4(a) shows that the CNTs grown at 650°C for 40 min are comparatively thin, and not as fully synthesized as those grown for 60 min (Fig. 4(b)). On increasing the reaction time the synthesized CNTs founded to be more entangled and close networks overall carbon templates. According to the FE-SEM image results, CNTs

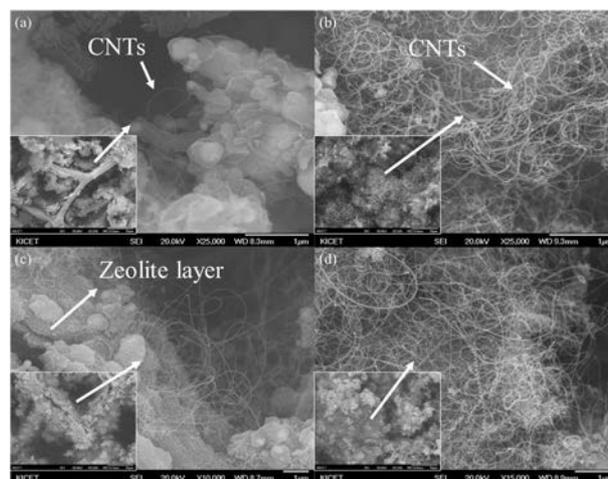


Fig. 4. FE-SEM micrographs of CNTs synthesized on BCT at 650°C for (a) 40, (b) 60, (c) 120 and (d) 180 min.

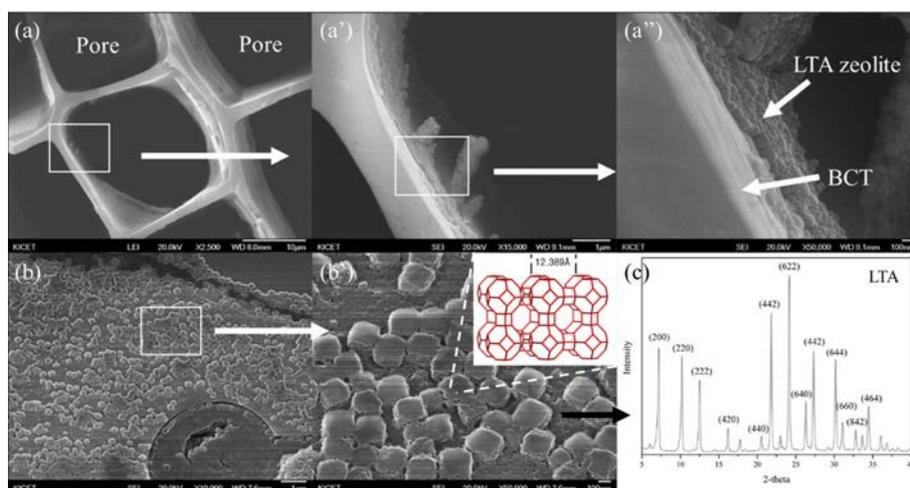


Fig. 3. FESEM image of zeolite-coated biomorphic carbon template (ZCBCT) and XRD pattern of zeolite crystal.

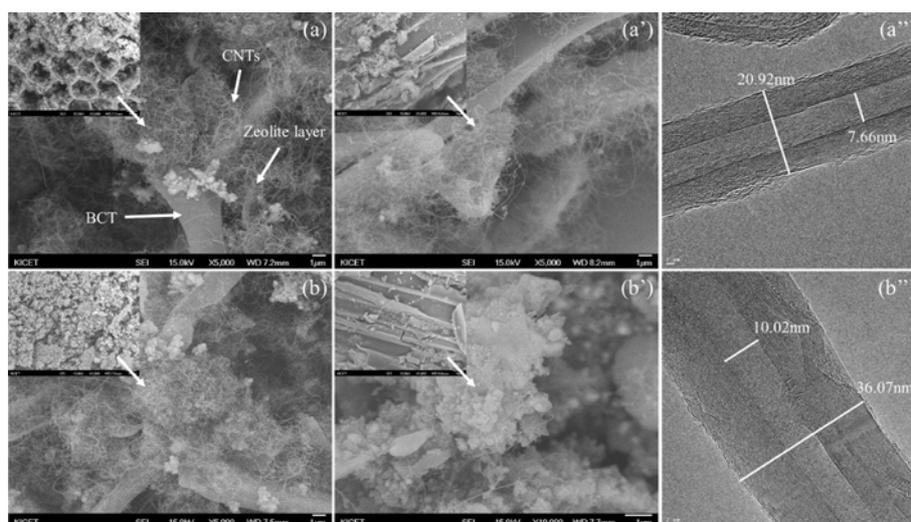


Fig. 5. FE-SEM and HR-TEM images of CNTs grown for 60 min at (a) 650, and (b) 700 °C

synthesized at a growth temperature of 650 °C are sufficiently full grown. As described by these images.

Fig. 5(a), (a'), (b) and (b') shows FE-SEM and HR-TEM images of multi-walled CNTs grown for 60 min at 650 and 700 °C, respectively. The CNTs synthesized on the BCT keeping zeolite as a base is clearly shown in Fig. 5(a), (a'), (b) and (b') for the FESEM images in vertical and horizontal view, respectively. The HR-TEM images in Fig. 5(a'') have a comparatively small outer wall, which forms a densely-layered structure with an outer diameter of around 20.92 nm. A base growth mechanism can be clearly seen in the CNTs, which are known for having better attachment tendencies to the substrate. The CNTs in the TEM images of Fig. 5(b'') show thicker outer walls, with a diameter of around 36.07 nm. Also, note here the apparent growth in terms of the inner and outer diameter of the nanotubes. Hence, it can be inferred that the decomposition of carbon atoms from C_2H_2 , which forms coaxial cylindrical graphene sheets layer by layer around the CNT core, strongly relates to the reaction time and temperature. All the CNTs samples display bamboo-like structure and are typically multi-walled CNTs.

Fig. 6 shows the TGA curves of the CNTs grown at 650 °C for (a) without CNTs, (b) 40 min, (c) 60 min, (d) 120 min and (e) 180 min, respectively. All samples represent an initial weight loss tendency, which may occur through the loss of physically adsorbed water by the zeolites until 195 °C. In the continuous increment of reaction time, all samples undergo a weight loss pattern. As compared with Fig. 6(a), all CNTs samples shows the weight loss i.e. (b) 2.8%, (c) 5.61%, (d) 6.95% and (e) 7.03%, respectively. These difference of weight loss can be explained with carbon yield.

The carbon yield from CNTs synthesized by metal-containing CCVD is calculated as follows:

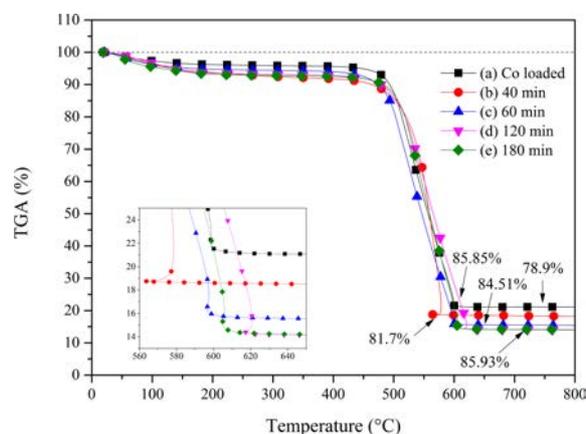


Fig. 6. TGA curves of the synthesized CNTs on biomorphic carbon template at 650 °C for (a) Co loaded, (b) 40 min, (c) 60 min, (d) 120 min and (e) 180 min.

Carbon yield (%) = $(m_{\text{tot}} - m_{\text{cat}}) / m_{\text{cat}} \times 100\%$ (1)
 where, m_{cat} is the initial catalyst amount (before reaction), and m_{tot} is the total sample weight after synthesis [15]. The TGA curves allow estimate of the amount of carbon yield. Table 1 shows the estimated amount of carbon yield.

Fig. 7 shows the Raman spectra of the synthesized CNTs. In this results, two strong peaks can be observed within the wavelengths 1340 cm^{-1} and 1600 cm^{-1} , designated as D- and G-bands, respectively. These represent the presence of impurities and defects in the graphitic sheets, and crystalline graphite carbon [13, 14]. The strength of the D-band relative to the G-band is a measure of the amount of disorder in the CNTs and is used for qualitative analysis of the nanotubes. The relative intensities of the D- to G- bands (the I_D/I_G ratio), as revealed by the Raman spectroscopy, which is a measure of the degree of graphitization is shown in Table. 1. The I_D/I_G values from this work are between 0.59 and 1.00, which is in accordance with those

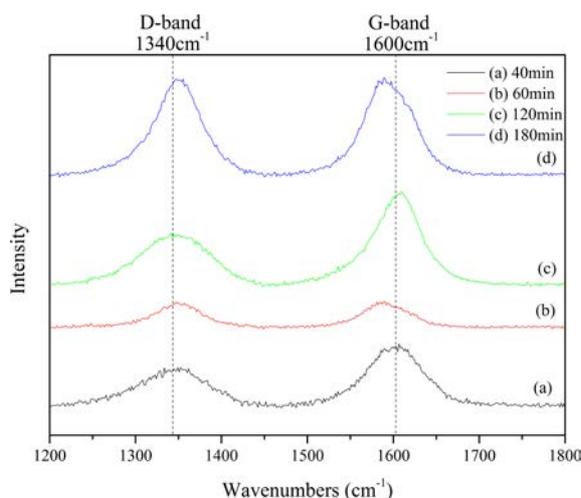


Fig. 7. Raman spectra of synthesized CNTs biomorphic carbon template for 60 min at (a) 650, and (b) 700 °C.

Table 1. Quality of CNTs (Raman spectra) and Carbon yield (TGA) for 60 min with respect to reaction temperature.

Sample name	Reaction temperature [°C]	Raman ratio [I_D/I_G]	Carbon yield [%]
40 min	650	1.00	2.8
60 min	650	0.81	5.61
120 min	650	0.98	6.95
180 min	650	0.59	7.03

reported in the literature ($I_D/I_G = 0.7-1.3$) for CVD-grown MWNTs [15, 17], revealing the high-quality CNTs grown in this experiment.

Conclusions

Carbon nanotubes (CNTs) synthesized on Co-supported zeolite coated biomorphic carbon template (CZBCT) were achieved with both high quality and high yield of carbons. The amount of MWCNTs were formed by the combination of three different novel processing routes. Because of the uniform pore structure, the zeolite crystals can be located all over the template surface. And also owing to high porosity zeolite crystals, the acetylene can supply carbon source to the catalytic metal nanoparticles appropriately to lead the growth of CNTs across the entire template. The morphology of CNTs was influenced by reaction temperature. The microstructure obtained at 700 °C exhibit a considerable wall thickness, and the widest inner hollow tube structure, whereas that of CNTs obtained at 650 °C shows comparability thinner outer wall and narrow inner hole. The maximum yield of carbon was 7.03% with the reaction time for 180min. but on comparing with the Raman ratio the synthesized

CNTs were found better quality at 60 to 120 min. with a higher yield of carbon. The Raman ratio shows the value of 0.59 to 1.00 which are within the range of values reported in the literature of $I_D/I_G = 0.7-1.3$ for CVD-grown MWCNTs

Acknowledgments

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