

## Synthesis of carbon nanotubes on zeolite coated biomorphic template

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A novel approach by the application of three different reaction technique was used for the formation of carbon nanotubes (CNTs) onto biomorphic carbon template. Carbon template having pore dimensions of 25  $\mu\text{m}$  was developed by carbonizing reaction. LTA zeolite crystals of 0.3  $\mu\text{m}$  were simultaneously synthesized within and coated the porous carbon template by an *in situ* hydrothermal process, and were subjected to a colloidal process to prepare the suitable catalyst nanoparticle for carbon nanotube synthesis. To grow CNTs within the carbon template a catalytic chemical vapor deposition (CCVD) technique was used, and the effects of reaction time and temperature on the morphology crystallinity, and yield of CNTs were investigated.

**Key words:** Carbon nanotubes, Novel process, Biomorphic carbon template, Zeolite, CCVD.

### Introduction

Since Iijima's discovery reported in 1991, carbon nanotubes (CNTs) have attracted the attention of researchers, because of their unique physicochemical properties dependent on the nanostructures [1]. In addition of their outstanding mechanical and electrical properties, CNTs also have a very high thermal conductivity and high specific surface area [2-4], which allow their use in a range of applications, including nano-electronic devices, field emission devices, composite materials, hydrogen storage materials, and filter materials [5, 6].

Because these applications are related to the high quality CNTs, their synthetic methods have always been significant [7]. Various processing routes for the synthesis of CNTs have been developed, which includes laser evaporation [8], arc-discharge [9] and chemical vapor deposition (CVD) [10]. The catalytic CVD has proven to be more efficient and promising for the synthesis of CNTs due to its simple operating conditions, low costs and high-yield production ability [11]. In general, CNTs are synthesized on catalyst containing metallic nano-particles (Fe, Co, Ni, Cu etc.) or related oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{MgO}$ , Zeolite etc.), by CCVD using carbon source ( $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ ,  $\text{C}_2\text{H}_4$ , etc.) [12]. Basically, CNTs researchers know how to make nanostructured materials from individual CNTs, but not enough study of CNTs-composites to bulk structure [13].

As might be expected, natural evolution through the ages has provided biological bulk materials with unique and sophisticated structures from renewable resources such as wood. Through pyrolysis of natural wood, a carbonaceous perform can be produced with fine hierarchical porous structure, ranging from millimeter via micrometer through to nanometer scale [14, 15]. At the same time, the resource of wood is abundant and different species of wood exhibits a large variety of available pore structure for the applications including filters, catalyst support, and porous ceramics [16]. The use of wood provides an inexpensive starting material having nearly net like and complex shape capabilities, instead of the simple shapes that are normally produced by material processing techniques [17].

The formation of CNTs within the Co ions supported zeolites coated biomorphic carbon template by CCVD is reported in this study. The novelty of this approach lies in the successive application of three different processing techniques, for the formation of the CNTs-composites. Firstly, with carbonizing reaction biomorphic carbon template (BCT) was. Then secondly, LTA zeolites were synthesized within and simultaneously coated the carbon template, which was then subjected to colloidal process resulting in the formation of Co catalyst-loaded zeolites-coated carbon template. Finally, with CCVD method CNTs were synthesized at 600-700  $^{\circ}\text{C}$ , and a CNTs synthesis was investigated varying reaction time (40, 60, 120 and 180 min). The effects of reaction temperature and time on the morphology and yield of CNTs were investigated. The synthesized CNTs-carbon matrix was analysed for microstructural properties and crystallinity, and the yield percentage was also estimated by TGA and Raman spectra.

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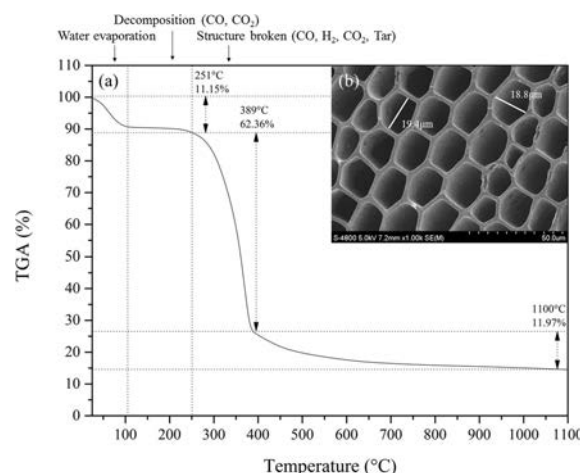
## Experimental

### Raw materials

Sapwood of Japanese cypress (*Chamaecyparis obtusa*) was used to carbonize honeycomb type porous carbon templates. Aluminium isopropoxide (AIP, 98+%), tetramethyl ammonium hydroxide (TMAOH, 25% hydroxide solution), tetraethyl orthosilicate (TEOS, 98%) and Sodium hydroxide pellets (NaOH, 99.998%), from Sigma-Aldrich and were used to produce LTA zeolite crystal. The metal catalyst Cobalt chloride hexahydrate ( $\text{CoCl}_2 \cdot 6\text{H}_2\text{O} \geq 99.0\%$ , Samchun Cemics) was used and for the carbon source, acetylene ( $\text{C}_2\text{H}_2$ , Kyuonin Chemical Industry) was used. In addition Nitrogen ( $\text{N}_2$ , 99.99%, Doekyang Co. Ltd), double de-ionized water and Ethanol ( $\text{EtOH}$ , 94.5%, Samchun Chemicals) were also used during the experiment.

### Preparation of biomorphic carbon template

The preparation of BCT includes two steps. First, a carbon template was prepared using the pyrolysis of Japanese cypress specimens in an inert atmosphere. To avoid the collapse of the specimen structure during the carbonizing process, the specimens were slowly heated up to 600 °C at the heating rate of 0.5 °C/min for 6-8 hrs in a horizontal electric furnace in  $\text{N}_2$  gas flow (10  $\text{cm}^3/\text{min}$ ). Subsequently, the temperature was increased to 1,000 °C at the rate of 3 °C/min to obtain a porous carbon template. Fig. 1(a) shows that,  $\text{H}_2\text{O}$ ,  $\text{CO}_2$ , acids, carbonyl groups and alcohols are released during the pyrolysis due to decomposition of biopolymer structures at temperatures up to 600 °C. Meanwhile, the cell wall materials of the natural wood was rearranged to convert it into the carbon structure. Under pyrolysis at the initial stage ( $T \leq 250$  °C), the water evaporation and decomposition of CO and  $\text{CO}_2$  starts with the weight loss of 11%, and then the structure of wood breaks ( $\text{CO}$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ), and changes into charcoal having 30% tar between 300 and 500 °C with the weight loss of 80% [17]. Fig. 1(b) shows that the unique anatomical features of the native means tissue can be retained

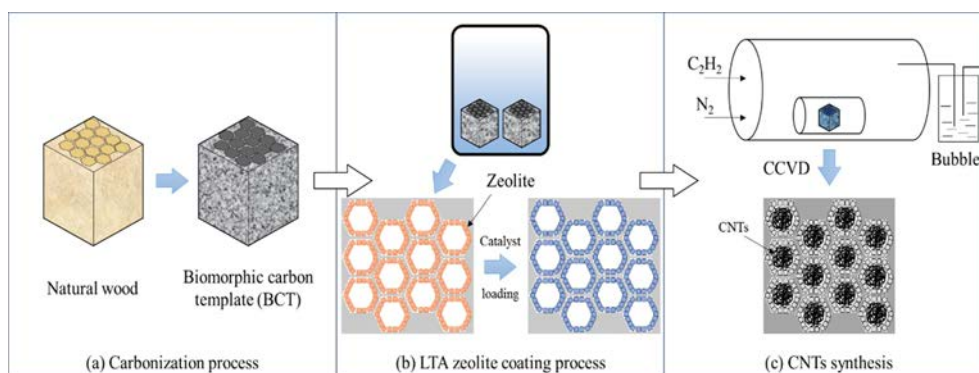


**Fig. 1.** TGA curves and FE-SEM image of carbonized biomorphic carbon template.

during pyrolysis, which yields a porous template that is primarily composed of honeycomb carbon structure.

### Zeolites synthesis, coating, and catalyst loading

To synthesize the LTA zeolites, a mother solution was prepared with a molar composition of AIP: TEOS : TMAOH : NaOH :  $\text{H}_2\text{O}$  of 1 : 2.2 : 2.4 : 0.3 : 200 stirring for 12 hrs. The BCT was immersed into the zeolite mother solution, and aging for 12 hrs. Afterward, the immersed BCT with zeolite mother solution was shifted into the teflon-lined stainless steel autoclave, and was proceeded with hydrothermal treatment at 90 °C for 72 hrs, as Fig. 2(b) shows. The zeolite-coated biomorphic carbon templates obtained were then subjected to dispersal by colloidal processing them into an aqueous  $\text{CoCl}_2$  solution (metal content  $\sim 0.8$  mmol). In this process, the Co ions from aqueous  $\text{CoCl}_2$  solution were supported on the template. This template was dried for 12 hrs. at room temperature, and was calcined in a tube furnace at 450 °C for 4 hrs in  $\text{N}_2$  atmosphere. The Co-supported zeolite-BCT was designated as CZBCT.



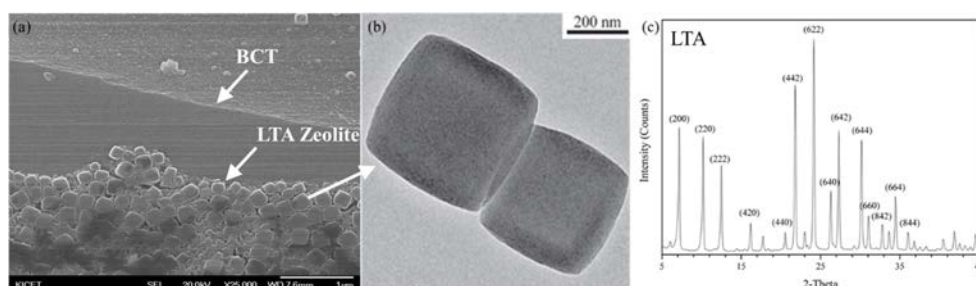
**Fig. 2.** Schematic diagram of the novel processing of synthesis CNTs on BCT: (a) Carbonization process, (b) LTA zeolite coating process, and (c) CNTs synthesis.

### CNTs synthesis

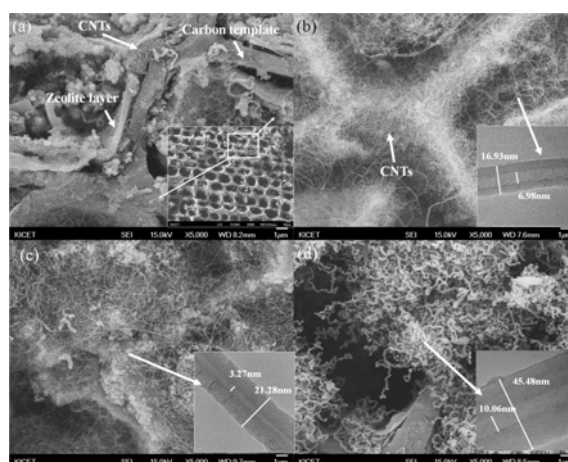
Fig. 2(c) shows that catalytic decomposition of acetylene on the CZBCT sample was carried out in a quartz boat centered in a horizontal tube furnace. The temperature was elevated with 5 °C/min to the desired reaction temperature in a nitrogen atmosphere (450 sccm). Carbon nanotubes were synthesized by CCVD method using  $C_2H_2$  gas as a carbon source (10 sccm). CNTs were separately synthesized at 650 and 700 °C for 40, 60, 120, and 180 min, respectively, using  $N_2$  carrier gas.

### Results and Discussions

Fig. 3(a) shows an FE-SEM image of BCT, which was used as the basic substrate for CNTs synthesis. Fig. 1(b) shows that the microstructure of the template obtained displays a hexagonal shape cell structure with 18.8~23.7  $\mu m$  range pore size (long side\*), and 2.3  $\mu m$  cell wall thickness. The morphology of the LTA zeolite crystals seen in the SEM image shows a cubic form comprised of well-controlled crystals of about 130 nm in size, as Fig. 3(a) shows. These images show not only high crystallinity but also perfect crystal morphology. The TEM image of Fig. 3(b) shows the crystal structure of LTA zeolites homogeneously synthesized and coated on the surface of the template by an *in situ* hydrothermal method. The LTA zeolite crystal shape was obviously of cubic form, with the crystal size of 300–400 nm. In general, the framework of LTA zeolite crystals can be described in terms of two polyhedral type; one with simple cubic arrangement of eight tetrahedral, also known as D4R; the other one is a truncated octahedron of 24 tetrahedral or cages. [18]. The LTA zeolite is generated by placing the D4R units with an experimental lattice constant of 12.389 Å, as shown in Fig. 3. These well-shaped zeolite crystals are excellent host and template materials that have an ordered framework structure with regular cages and channels of sub-nano size (4 Å) for nano-crystal, quantum dots (1–10 nm), and also act as nano-catalyst for the formation of CNTs [19]. Fig. 3(c) shows 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.

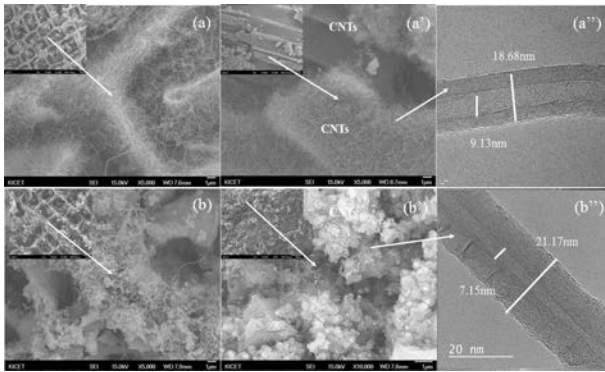


**Fig. 3.** (a) FE-SEM image of zeolite coated biomorphic carbon, (b) TEM image of LTA zeolite, and (c) XRD pattern of zeolite crystal.



**Fig. 4.** FESEM and TEM images of CNTs synthesized at 650 °C for (a) 40, (b) 60, (c) 120, and (d) 180 min, respectively.

Fig. 4 shows FE-SEM and corresponding TEM images in the inset of CNTs that are synthesized on CZBCT by the CCVD method at 650 °C for 40, 60, 120 and 180 min, respectively. CNTs synthesized on both, the CZBCT surface and inside the pores are clearly observed in the FE-SEM images. Moreover, an intense CNT growth can be observed over the cell wall surface. Fig. 4(a) shows that the CNTs grown at 650 °C for 40 min are comparatively thinner, and are not fully synthesized when compared to those grown for 60, 120 and 180 min, CNTs were grown in large numbers and are seen to have formed a very close network structure by entangling with each other all over carbon templates. Through a comparison, it can be easily found that all the synthesized CNTs were MWCNTs with inner diameters within 10 nm. However, a monotonic increase with prolonging reaction time is clear evident from Fig. 4, which corresponds to the increasing thickness of CNTs walls of 16.93, 21.28 and 45.48 nm for 60, 120, and 180 min, respectively). Also, from the FE-SEM images, the CNTs synthesized at 650 °C for 60 and 120 min was found to be better in terms of outer wall smoothness and the hollow tube-like characteristics. While comparing with the others synthesized at 40 and 180 min. Therefore, the 60 min and 120 min reaction time are considered appropriate for CCVD synthesis of CNTs at 650 °C.



**Fig. 5.** FESEM and TEM images of CNTs synthesized at (a), (a'), (a'') 650 °C and (b), (b'), (b'') 700 °C for 60 min, respectively.

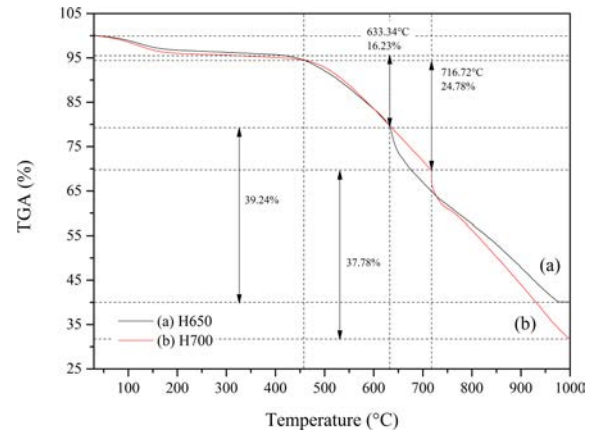
Fig. 5 shows FESEM and TEM images of CNTs grown for 60 min with at 650 and 700 °C, respectively. As in Fig 5(a) the CNTs grown at 650 °C shows specific characteristics with smooth outer wall as well as inner wall giving hollow tube like structure. Whereas, CNTs shown in Fig. 5(b) CNTs grown at 700 °C have comparatively thick layered outer walls, with a diameter of around 21.17 nm. Therefore, it can be inferred from here that the decomposition of carbon atoms from  $C_2H_2$ , which forms MWCNTs which is directly proportional to the reaction temperature [18]. In accordance with the above inference, all the CNTs samples display bamboo-like structure, and are typically MWCNTs and at 650 °C was showing better yielding properties (Table 1).

Figs. 6(a) and 6(b) show the TGA curves of the CNTs grown for 60 min at 650 and 700 °C, respectively. All CNTs samples represent an initial weight loss tendency, which may occur through the evaporation of the adsorbed water by the zeolites until 195 °C [19]. In the subsequent heating process, both (a) and (b) samples undergo a two-step weight loss pattern. In the first step (458–633 °C and 485–717 °C, respectively), the amorphous carbon has been combusted, and in the second step ( $\geq 633$  °C and  $\geq 717$  °C, respectively), the MWCNTs have been combusted until 800 °C. After that, the samples maintain a weight loss pattern due to biomorphic carbon combustion. The main reason for the two-step pattern is that the decomposition of carbon source on Co-catalyst leads to the formation of CNTs as amorphous carbon [18, 19]. The carbon yield from CNTs synthesized by metal-containing CCVD is calculated as follows:

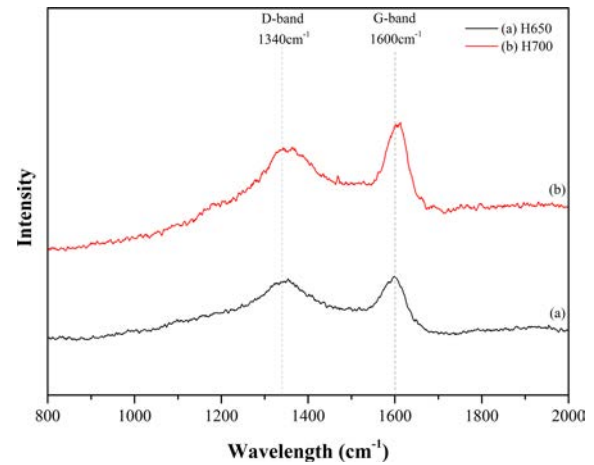
$$\text{Carbon yield (\%)} = (m_{\text{tot}} - m_{\text{cat}}) / m_{\text{cat}} \times 100\% \quad (1)$$

where,  $m_{\text{cat}}$  is the initial catalyst amount (before reaction), and  $m_{\text{tot}}$  is the total sample weight after synthesis [20]. 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 all spectra, two strong peaks can be observed



**Fig. 6.** TGA curves of the synthesized CNTs on biomorphic carbon template for 60 min at (a) 650, and (b) 700 °C.



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

**Table 1.** Characterization of Raman ratio and Carbon yield for 60 min with respect to reaction temperature.

| Sample name | Reaction temperature [°C] | Raman ratio [ $I_D/I_G$ ] | Carbon yield [%] |
|-------------|---------------------------|---------------------------|------------------|
| H650        | 650                       | 0.99                      | 18.72            |
| H700        | 700                       | 0.98                      | 9.98             |

around the wavelengths  $1340\text{ cm}^{-1}$  and  $1600\text{ cm}^{-1}$ , designated as D- and G-bands, respectively. These indicate the presence of impurities and defects in the graphitic sheets, and crystalline graphite carbon, respectively [20]. The relative intensity of the D- and G- band is a measure of the amounts of defects in the MWCNTs and is used for qualitative characterizations of the carbon nanotubes. Table 1 also provides the relative intensities of the D- to G- bands, the degree of graphitization was characterized by Raman spectroscopy. The  $I_D/I_G$  ratio from this analysis was found between 0.98 and 0.99, which is in accordance with those reported in the literature ( $I_D/I_G = 0.7\text{--}1.3$ ) for CVD-grown MWNTs [21, 22], revealing the high-quality CNTs grown in this experiment.

## Conclusions

CNT-biomorphic carbon template having a large amount of MWCNTs were synthesized by a novel processing route that unified three independent processing techniques in succession. Owing to the high porosity of both the template and the LTA zeolites, the  $C_2H_2$  supply to the catalytic metal nanoparticles was very easy, leading to the growth of uniform and dense CNTs across the entire BCT. Both ranges of time and temperature were investigated, and 650 °C was chosen as the optimum temperature for the highest carbon yield of CNTs of about 18.72%. The results show the dramatical difference in morphology, yield content, and crystallinity with in various reaction temperature. The microstructure obtained at 700 °C temperature shows considerable wall thickness, and the narrow inner diameter in tube structure. The relative intensities of the D- to G- bands, the degree of graphitization was characterized by Raman spectroscopy. The  $I_D/I_G$  ratio from this analysis was found between 0.98 and 0.99, which is in accordance with those reported in the literature ( $I_D/I_G = 0.7$ -1.3) for CVD-grown MWNTs. Finally, the CNTs composite materials can be a good candidate as nano-filter application for next generation.

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