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SYNTHESIS OF MULTI-WALLED CARBON NANOTUBES (MWNTS) OVER ANODIC ALUMINUM OXIDE (AAO) TEMPLATE

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Abstract Currently ordered carbon nanotube (CNT) arrays are generally prepared using the template synthesis method. The template synthesis method can improve the selectivity and uniformity of CNTs. Therefore in this study, the AAO templates were applied as the catalyst support to synthesize CNTs in high yield and cost saving by controlling the CNTs characteristics and morphologies. A practical and high performance CCVD system was designed and built to carry out the pyrolysis of hydrocarbon to produce the multi-walled carbon nanotubes (MWNTs). The supported catalysts of cobalt (Co), iron (Fe) and mixture of Co and Fe were prepared using the AAO template as the support. The AAO supported catalysts were prepared using the wetness impregnation method. The characterizations of the MWNT yields were carried out using Scanning Electron Microscope (SEM) and Transmission Electron Microscope (TEM) as well as Energy Dispersive X-ray Analysis (EDX). The AAO supported catalysts prepared were found capable of producing good quality MWNTs and generated carbon content as high as 86.5 wt%. The as-grown MWNTs showed high degree of graphitization, purity and density with configurations of bundles, arrays and coils.

KERWORDS: Multi-walled carbon nanotubes (MWNTs), anodic aluminium oxides (AAO) template

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Introduction

The main hindrance in employing carbon nanotubes (CNTs) in the real world is the inability to control the growth of the nanotubes and to grow carbon nanotubes in large amount. Recently, the catalytic chemical vapour deposition (CCVD) has been widely used by applying various supported metals catalysts in the production of CNTs. Being a catalytic process, the combinations of transition metals and support can be changed depending on the characteristics required.

Porous anodic aluminum oxide (AAO) templates were prepared electrochemically from aluminum metal. These membranes are unique materials, with a high density of straight, cylindrical pores (up to 10^{11} pores/cm^2) of a very uniform size, and can be obtained with different pore sizes ranging from 5 nm to more than 200 nm (Fuertes, 2002). These nanopores constitute an ideal host for carrying out the synthesis of nanomaterials because of their special characteristics. The template synthesis method enables high-density arrays of well-aligned carbon Nanotubes of a similar diameter, wall thickness and length to be prepared (Li *et al.*, 2003). The CNTs arrays perfectly copy the three-dimensional structures of the nanochannel in the template, where the resulting outer diameter of the CNTs matches the inner diameter of the channels. The CNTs growth in AAO template is one of the more promising approach owing to the possibility of tailoring the size and density of the AAO template pores.

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Methodology

Anodic aluminum Oxide (AAO) template (Whatman Anodisc 47, 200 nm diameter pores and 50 μm thickness) was used as the catalyst support of cobalt (Co), iron (Fe) and Co-Fe mixture by applying dip coating technique of impregnation method. The Co and Fe metal salt was used as the catalyst precursors. The synthesis of CNTs was carried out using a home-built Catalytic Chemical Vapour deposition (CCVD) system. Further details of the CNTs synthesis parameters have been reported elsewhere (Tee *et al.*, 2004). The characterizations of the CNT yields were carried out using Scanning Electron Microscope (SEM), Transmission Electron Microscope (TEM) and Energy Dispersive X-ray Analysis (EDX).

Results and Discussion

SEM and TEM Analysis

The AAO supported catalysts were prepared and used in the production of MWNTs. The SEM micrographs revealed that forest of CNTs grown on the surface of the AAO/Co catalyst template as depicted in Fig. 1 (a). A few coiled CNTs also grew on the AAO/Co catalyst as the Co catalysts can enhance the growth of coiled CNTs (Lu *et al.*, 2004). From Fig. 1 (b), the cross sectional view of the yields showed that the CNTs were observed to grow on the wall of the AAO-Co catalyst template. Conversely, the density of CNTs on the template surface was decreased when the AAO-Fe catalyst was applied. However, the nanotubes were detected to have grown from the Fe catalyst layer on both the surface and wall of the nanochannels of the catalyst as depicted in Fig. 2 (a) and (b) respectively.

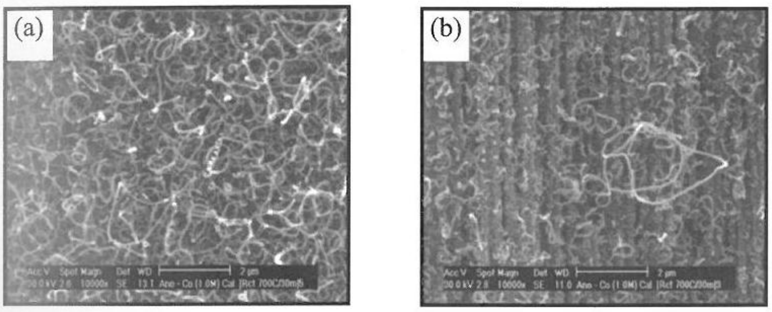

Figure 1. SEM micrographs of CNTs grown over AAO/Co template catalyst, (a) surface and (b) cross section

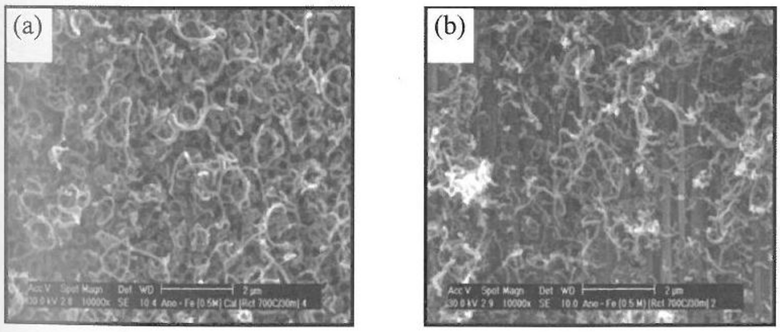

Figure 2. CNTs grown over AAO/Fe catalyst, (a) surface and (b) cross section

However, the AAO/Co-Fe catalyst showed the best activity by growing CNTs with two types of growth pattern: (i) Fig. 3(a) showed the CNTs bundles grown on the template surface and (ii) Fig. 3(b) showed the arrays of CNT extruded from the inside of the nanochannels. The pairing of Co and Fe also promoted the growth of aligned CNTs as reported by Mukhopadhyay and Mathur, (2004). The alumina in AAO template itself is a catalyst in the hydrocarbon decomposition process due to the Lewis acid nature of its surface sites. Jing *et al.*, (1998) reported that the CNTs are formed by the joint catalytic activities of metal particles and alumina walls.

The CNT yields grown over the AAO/Co-Fe catalyst are classified as MWNTs since the hollow structure and the turbostratic wall layers of MWNTs was clearly depicted in the TEM images. In Fig. 4 (a), the CNT has straight and turbostratic walls, only the most external layer appears jagged and curved. Figure 4 (b) attested that the as-grown MWNT over AAO/Co-Fe catalyst has superb characteristic with very high purity and graphitization. The carbon building units are arranged in an orderly fashion to produce extremely turbostratic and defect-free graphene layers. The inner diameter is 3.57 nm whereas the outer diameter is 11.43 nm with the distance between layers measured as 0.33 nm.

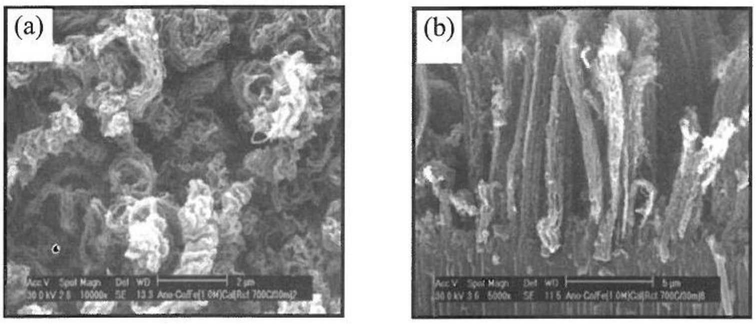

Figure 3. SEM micrographs of CNTs grown over AAO/Co-Fe template catalyst, (a) surface and (b) cross section

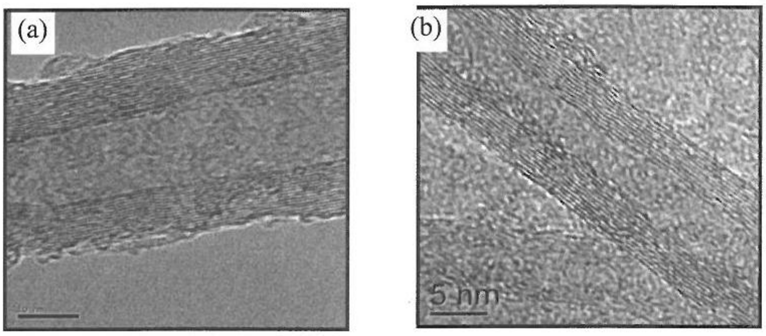

Figure 4. TEM micrographs of MWNT grown over AAO/Co-Fe catalyst template

Energy Dispersive X-Ray (EDX) Analysis

The EDX analysis data showed that the carbon composition of the MWNT yields varied from 34.2 to 86.5 wt%, as shown in Table 1. The AAO/Co catalyst generated higher carbon composition than the AAO/Fe catalyst. However, the AAO/Co-Fe catalyst produced highest the carbon composition attributed to the two types of nanotubes growth pattern.

Table 1. EDX analysis data of carbon composition (wt%) of as-grown MWNTs

Template Catalyst	Carbon Composition (wt%)
AAO/Co	73.1
AAO/Fe	34.2
AAO/Co-Fe	86.5

Conclusion

The ability to produce CNTs was vary in the order of Co/Fe > Co > Fe catalysts. The Co catalysts are effective in forming coiled CNTs whereas the bimetallic catalysts accountable for the alignment of CNTs.

Acknowledgements

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