Synthesis and characterisation of larger diameter multi-walled carbon nanotubes over anodic titanium oxide template

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The well known fascinating properties of carbon nanotubes (CNTs) stimulated the researchers to make extensive efforts to control their growth and properties. Different growth techniques including arc discharge [1], plasma technique [2], laser ablation [3] and pyrolysis of hydrocarbon over catalyst [4] have been used to control the position, direction and arrays of CNTs. Recently, the formation of carbon nanotubes over porous templates such as anodic aluminum oxide (AAO) inspired a new way to obtain well ordered CNTs with uniform size and shape [5,6]. Many reports are available on the confined formation of CNTs inside the pores of AAO with and without metal catalyst using propylene, acetylene, and polyphenyl acetylene as carbon source [6–8]. Naturally, the question arises whether other value metals such as Ti, Ta, Nb, V, Hf and W can also be used to form the CNTs inside the pore arrays fabricated by anodization process similar to AAO. Among the oxides of other value metals, titanium dioxide is considered as a promising material for photocatalyst, catalyst support and implants [9,10]. The catalytic activity of Lewis acid sites of TiO_2 can be utilized for the growth of CNTs by pyrolysis of a suitable carbon rich hydrocarbon. Up to now no report is available on the usage of porous titanium oxide obtained by anodization, as template for the growth of CNTs. Hence, the aim of this study is to form CNTs by CVD method using acetylene as carbon source over porous titanium oxide template obtained by anodization process and to reveal the morphology and structural characteristics of the obtained CNTs using various instrumental techniques.

In this way, anodic titanium oxide (ATO) was obtained by anodization of commercially pure titanium metal in the mixture of 1 M H_2SO_4 and 0.5% HF, as electrolyte at a constant potential of 40 V for 72 h. The size and morphology of nanopores of ATO were analysed by SEM and typical top-view images are shown in Fig. 1. It is observed that more regular nanopores with diameter of 70–80 nm were formed. Also, the size of the nanopores is almost uniform with high density, which is beneficial for the formation of CNTs with uniform size.

The CNTs were formed over ATO template by CVD method using acetylene as carbon source with Ar as carrier gas at 650 °C for 2 h, followed by annealing at 600 °C for 15 h. The obtained CNTs were purified by treating with 23% HF for 30 h. The features of CNTs were studied by TEM and the representative images are shown in Fig. 2. It is clearly seen that CNTs of 70–80 nm in diameter with a wide, empty inner space were observed. The thickness of the walls of the CNTs is found to be thin and homogeneous. Also, the length of the CNTs is in the range of several micrometers. Further, most of the CNTs are found to be straight with very few of them having branches. The open-end structure of the tip is clearly noticed (Fig. 2b). Generally, the CNTs are open-end at top side and closed end at the bottom side. Further, the walls of the CNTs are smooth with homogeneous thickness indicating the uniformity of the internal surface of nanopores. The domelike structure (Fig. 2d) of the bottom of CNTs is reflecting the structure of so-called barrier layer, a thin oxidized layer separating the porous TiO_2 layer from the Ti metal substrate. When the CVD process is carried out at 650 °C, the decomposition of acetylene in nanopores results in carbon deposition on the surface of internal pore, which constitutes the tubes and copies the three-dimensional channel structure of the template. The formation of CNTs inside the ATO pores without any metal catalyst indicates that the catalytic behavior of the internal pore surface of TiO_2 plays an important role in the decomposition of acetylene, in addition to template function. Hence, it is assumed that the Lewis acid sites of the TiO_2 are responsible for the catalytic activity. Since anatase and rutile forms of titanium dioxide are widely used as catalyst,

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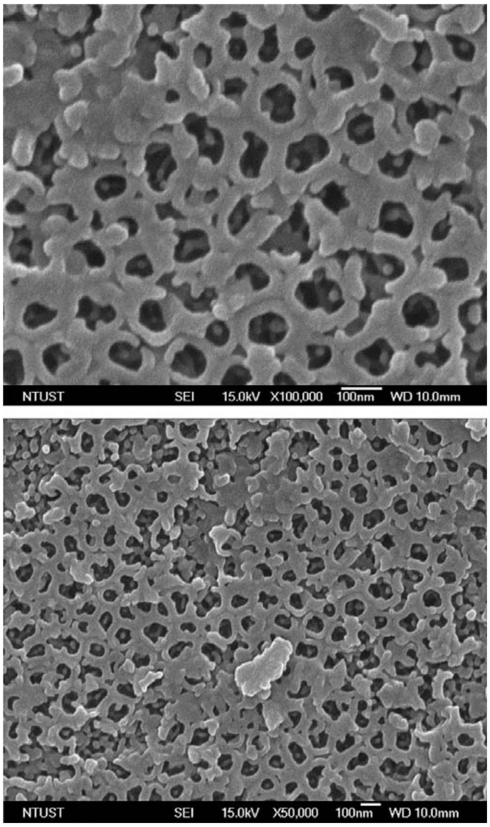

Fig. 1. Top-view SEM images of ATO template at different magnifications.

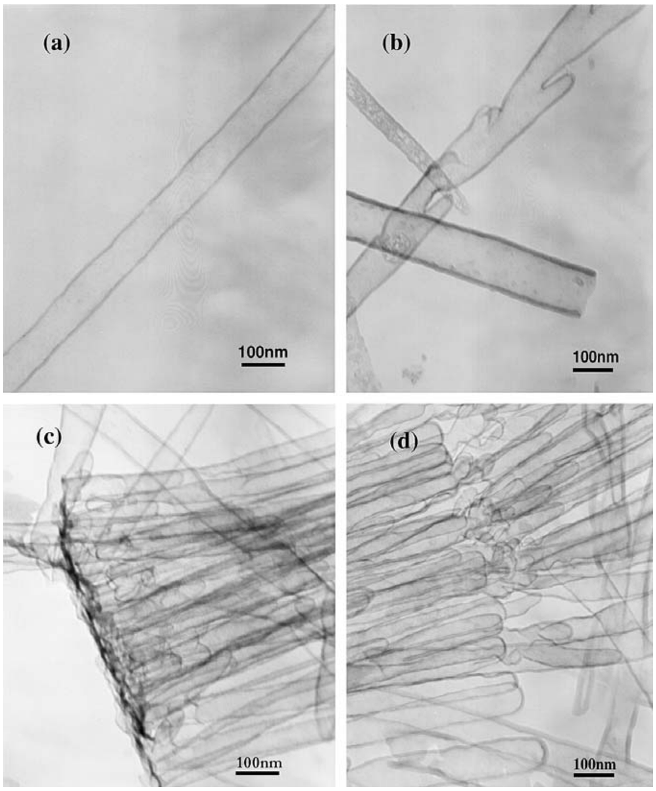

Fig. 2. TEM images showing different orientations of purified CNTs grown over ATO template.

catalyst support and photocatalyst in many chemical transformations, it is expected that the strength of Lewis acid sites of porous TiO_2 is high enough to catalyse the decomposition of acetylene at 650 °C. From the morphology of CNTs, it is assumed that internal surface of pores is uniform and hence uniform catalytic activity is expected. Therefore, the chance for the decomposition of acetylene is same at any point of the walls of nanopores and hence surface is uniformly covered by the carbon deposits during the CVD process, leading to the formation of carbon nanotube-like structure. Further, HRTEM measurements were also tentatively carried out to study the wall structure of the CNTs and the images are presented in Fig. 3. In spite of the amorphous background due to the specimen support film, tubes are found to be multi-walled. The wall thickness is in the range of 3 nm (Fig. 3a) for CNTs with deposition time of 2 h and it can be guessed on the image that the walls have 3–4 graphene layers with high quality nanotexture, i.e., graphenes do not show many distortions. That the CNTs are made of typical "turbostratic graphite" is likely [11,12]. It is interesting to note that the internal diameter of the CNTs is around 70 nm, which is different from

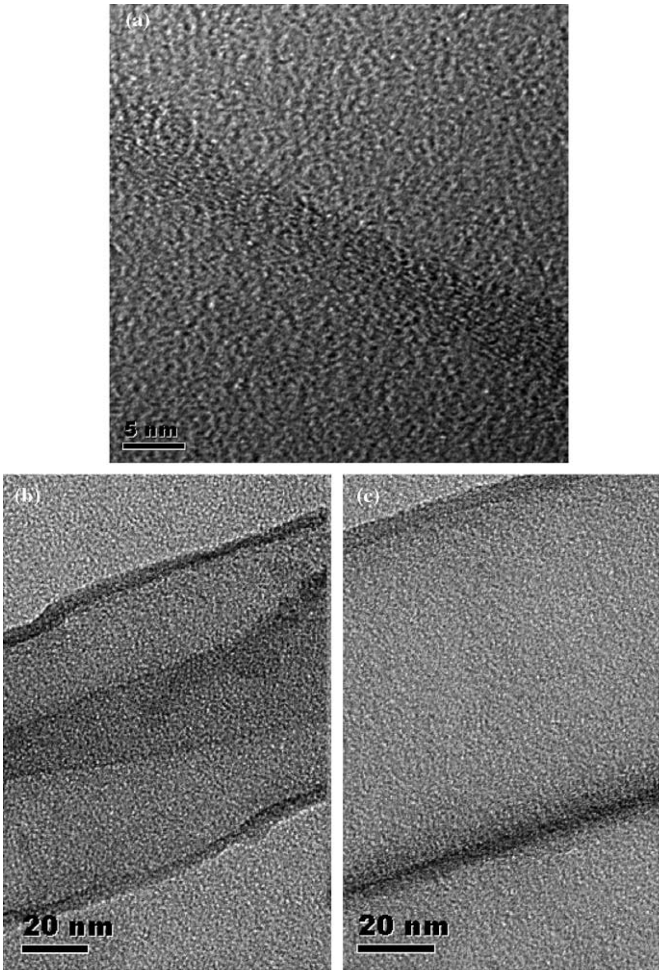

Fig. 3. HRTEM images showing the wall structure of CNTs grown with different deposition time; (a) 2 h; (b) 4 h and (c) 5 h.

that of CNTs grown over AAO [7], which is around 15–20 nm. This is due to the fact that only less number of graphene layers constitutes the walls of CNTs, as shown by HRTEM. The CNTs are formed on the inner surface of pores of ATO template due to the catalytic decomposition of acetylene on Lewis acid sites. The Lewis acid sites in the pores could act as a catalyst in forming of few walls of the CNTs. But, after the few walls are formed on the inner surface, the Lewis acid sites of ATO exist underneath the carbon nanotube walls. Due to this phenomenon, the Lewis acid sites of TiO_2 can not act as a catalyst anymore and the catalytic decomposition of acetylene stops, typically resulting in a very thin wall as opposed to CNTs made by other methods. In order to confirm the same, CNTs were grown with deposition time of 4 and 5 h under similar experimental conditions and the corresponding HRTEM images are presented in Fig. 3b and c, respectively. The wall thickness of CNTs in both cases is around 3–4 nm. When comparing with that of CNTs with deposition time of 2 h (Fig. 3a), no significant increase in wall thickness is observed. When increasing the carbon deposition time, the wall thickness of CNTs is not increased, indicating that the decomposition of acetylene is due to Lewis acid sites of TiO_2 and not due to thermal decomposition.

The thermal stability of the CNTs was studied by thermo gravimetric analysis (PerkinElmer TGA) using air as carrier gas. From the TGA curve (Fig. 4), it is observed that the CNTs were stable up to 550 °C and then the decomposition starts and reaches maximum loss at 628.5 °C. At around 641 °C, almost complete weight loss is seen showing the complete decomposition of CNTs. The single sharp exothermic peak indicates that only a single phase exists in the sample. The thermal stability of the grown CNTs in air atmosphere is found to be significantly higher than the value reported (480 °C) for CNTs grown by AAO with Co [13] and comparable (650 °C) with that of CNTs grown over FeMoMgO catalyst [14], but significantly lower than that of CNTs by arc-discharge method. The lower burning temperature of CNTs with respect to latter is related to the lesser number of layers in walls, their nanotexture quality and fact that the tubes are open-ended, meaning that graphene edges from the wall are easily accessible to the oxidizing gas.

The structure and vibrational modes of purified CNTs were analysed by XRD (X'Pert PRO-XRD) and Raman spectroscopy (Renishaw), respectively and are presented in Fig. 5. In XRD, two major peaks are observed, one is at $2\theta = 26°$ corresponding to 002 reflexion, that relates to the stacking order in polyaromatic solids. The other small asymmetric peak around 43.5° is due to 10 reflexion of turbostratic carbons. The Raman spectrum shows two strong bands at 1347 and 1592 cm^{-1} confirming the multi-walled nature of the CNTs. These bands are corresponding to fundamental vibration modes of D^4_{6h} of graphite [15]. The band at 1592 cm^{-1} (G band) corresponds to the Raman allowed optical mode E_{2g} of two-dimensional graphite, i.e., Raman active in-plane vibrational mode for an infinite or finite hexagonal network. The band at 1347 cm^{-1} (D band) is mainly derived from disordered carbon defects of the MWNTs, and is one of the in-plane vibrational modes.

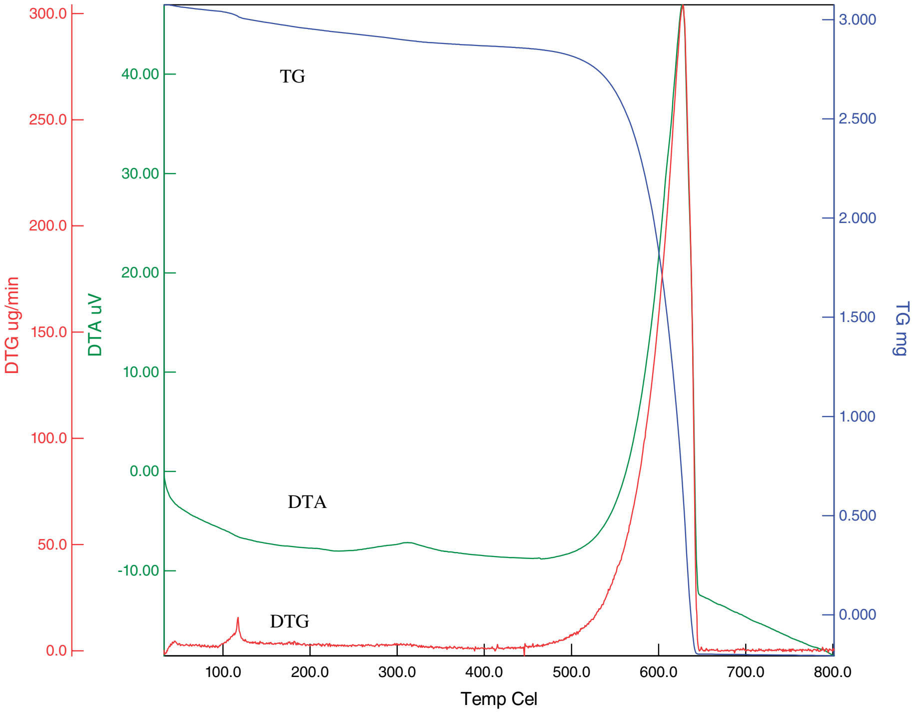

Fig. 4. TG and DTG curves of purified CNTs in air atmosphere.

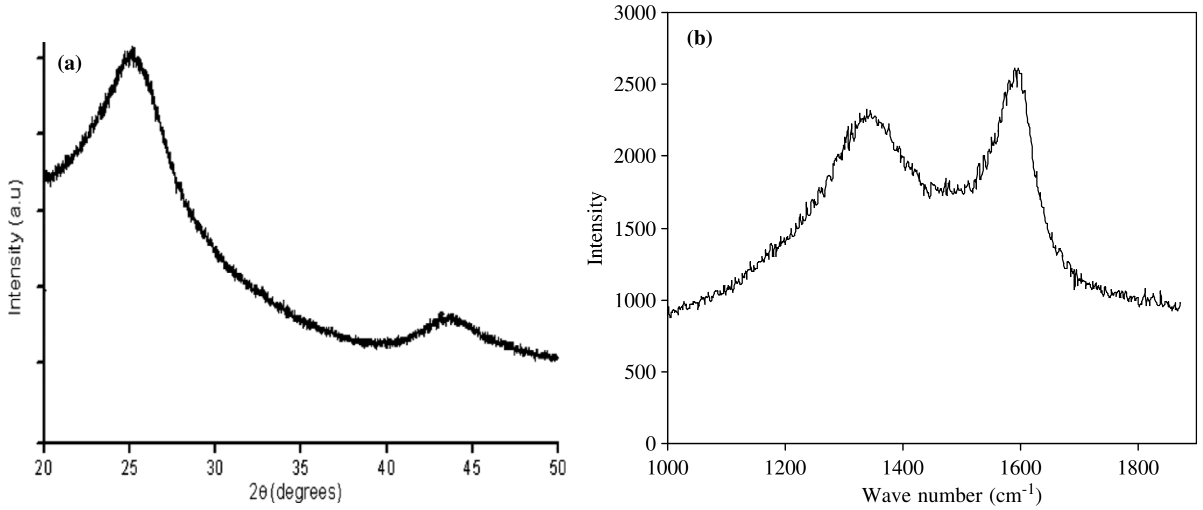

Fig. 5. XRD (a) and Raman spectroscopy (b) of CNTs grown over ATO template.

As compared to the G band at 1580 cm^{-1} for graphite, the shift in G band towards higher wave number (1592 cm^{-1}) as well as the I_D/I_G value (0.88) suggests a turbostratic structure, consistent with HRTEM and XRD investigations.

In summary, ordered CNTs with high nanotexture were formed, for the first time over anodic titanium oxide template and are hollow and straight. The catalytic activity of Lewis acid sites inside the pores of titanium oxide is strong enough to catalyse the decomposition of acetylene, leading to the formation of CNTs. The selective formation of CNTs over porous titanium surface could be used for the fabrication of nanofunctional devices. Also, the larger size of the CNTs favors higher metal dispersion as well as the accessibility of reactant molecules to metal particles inside the CNTs, when it is used as catalyst support in various chemical reactions.

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