Syntheses of Uniform Carbon Nanotubes by Chemical Vapor Infiltration Method Using SBA-15 Mesoporous Silica as Template

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A novel synthesis route has been developed to fabricate carbon nanotubes with superior yield and uniform diameters by chemical vapor infiltration method using Fe-catalyst supported on SBA-15 mesoporous silica as template.

1. INTRODUCTION
Carbon nanotubes (CNTs) have been extensively studied during the past decade owing to their potential applications in a variety of areas [1-5]. Various attempts have been made to manipulate the physical properties of CNTs using different strategies and synthesis conditions particularly in tailoring their diameters [6-10]. Despite of the complexity provoked during synthesis of CNTs by different CVD routes, the growth of ordered CNTs with tunable diameters were made possible by using anode aluminum oxides (AAOs) as templates [11]. Nonetheless, the aforementioned method normally results in only moderate product yield, which this study aims to improve. However, instead of using AAOs as catalyst supports, we employed SBA-15 mesoporous silica that possess a hexagonal pore structure with uniform and tunable pore size (5-30 nm) [12] to control the size of the catalyst particles. Two different methods, namely co-precipitation and impregnation, were used to prepare the supported iron (Fe) catalysts by which CNTs with uniform diameters were successfully fabricated by means of a chemical vapor infiltration (CVI) method [13] using C2H2/H2 gas mixture as the feed. Subsequently, the structural and physical properties of the supported Fe/SBA-15 catalysts and the resultant CNTs were characterized by powdered X-ray diffractometry (XRD), scanning/transmission electron microscopy (SEM/TEM), and N2 adsorption/desorption measurements.

2. EXPERIMENTAL
Mesoporous SBA-15 silica with an averaged pore size of 7.7 nm was prepared following the recipe reported earlier by Mou et al. [14]. The as-synthesized SBA-15 was subjected to calcination treatment in air at 823 K for 6 h to remove the surfactant occupied in the channels.

Two different methods, namely co-precipitation and impregnation, were adopted to incorporate the iron (Fe) catalyst particles into the channels of SBA-15 support. Supported Fe/SBA-15 catalysts prepared by co-precipitation method were carried out by stirring ca. 0.4 g of Fe(NO3)3(s) in suspended solution of SBA-15 (ca. 1 g) for 0.5 h in distilled water, followed by filtering and drying (at 373 K).
Subsequently, the resultant product was then subjected to reduction treatment under flowing H$_2$ (50 sccm) at 1073 K for ca. 10 min; these catalyst samples are hereafter denote as Fe(co)/SBA-15. On the other hand, samples prepared by impregnation method were obtained by the following procedures: first, Fe(NO$_3$)$_3$(aq) were prepared by dissolving ca. 0.4 g of Fe(NO$_3$)$_3$(s) in de-ionized water, then ca. 1 g of SBA-15 powder was added into the solution under extensive stirring, followed by evacuation treatment. Subsequently, the dried powder was stirred in CH$_2$Cl$_2$ solvent, to facilitate the migration of residual Fe(NO$_3$)$_3$(aq) into the pore channels of the SBA-15 [15], followed by removal of excess solvent by evacuation. This procedure was repeated once, then, the final product was subjected to reduction treatment under H$_2$ at 1073 K for ca. 10 min; these catalyst samples are hereafter denoted as Fe(im)/SBA-15.

Fabrications of CNTs were carried out by introducing the supported Fe(co)/SBA-15 or Fe(im)/SBA-15 catalyst in a home-made quartz reactor (volume ca. 30 mL), followed by CVI procedure under 1073 K; which was done by injecting C$_2$H$_2$/H$_2$ gas mixture under a flow rate of 50/50 sccm and ca. 2 kPa pressure. The resultant product was then digested with aqueous HF solution (1 M) with 50% ethonal-50% H$_2$O to remove the silica support, followed by filtering and drying.

All samples were examined by small-angle powder X-ray diffractometer (Philips X’Pert PRO) using CuKα (0.154 nm) radiation (40 kV, 30 mA) and verified by TEM on a JEOL JEM-2100 instrument operated at 200 keV. Prior to the TEM experiment, each powdered sample was first suspended in ethanol solution, followed by ultrasonic treatment for 0.5 h, then dispersed and dried on a copper grid. The physical properties of the samples were determined by N$_2$ adsorption/desorption isotherms (Micromeritics ASAP 2010) measured at 77 K.

3. RESULTS AND DISCUSSION

The TEM image of SBA-15 in Fig. 1a reveals that the parent sample possesses the expected well-ordered 2D hexagonal pore structure with uniform pore diameter of ca. 7.7 nm, in excellent agreement with the BJH pore size distribution obtained from N$_2$ adsorption/desorption measurements (not shown) and the XRD profile (Fig. 2a), which reveals characteristic (100), (110), and (200) peaks at 2θ angle of 0.93°, 1.54° and 1.75°, respectively.

As shown in Fig. 2b, the XRD pattern obtained for Fe(co)/SBA-15 shows characteristic diffraction peaks

Fig. 1. TEM images recorded alone the [110] plane of (a) parent SBA-15 and (b) Fe(im)/SBA-15. Insert: [100] plane of (a).
similar to that of its parent support with the exception that a notable decrease in the (100) peak intensity was evident, indicating that incorporation of Fe catalyst has little effect on the genuine 2D hexagonal structure of SBA-15. However, its TEM micrograph (not shown) revealed that majority of the Fe catalyst particles are deposited on the external surfaces of the support. On the other hand, the Fe(im)/SBA-15 prepared by impregnation method led to a well-dispersed, nano-sized Fe particles within the pore channels of the SBA-15, as illustrated by the TEM micrograph in Fig. 1b. Moreover, by comparing the XRD patterns of the parent SBA-15 (Fig. 2a) and Fe(im)/SBA-15 (Fig. 2c), it is clear that the latter exists only the (100) diffraction peak at 2θ ~ 1.0°, indicating that incorporation of Fe catalyst does have some effect on the local ordering of the structure. By comparing to the co-precipitation treatment, it is indicative that the impregnation treatment promotes migration of Fe precursors into the pore channels of the SBA-15 support and hence leads to well-dispersed Fe particles whose sizes are decided by the pore size of their parent SBA-15 support.

Further CVI process using the supported Fe(co)/SBA-15 and Fe(im)/SBA-15 catalysts both lead to formation of CNTs. Typically, the resultant CNTs product have excellent graphitic structure and an overall length greater than 12 μm, as respectively verified by Raman spectroscopy and TEM analysis (not shown). However, owing to the uncontrollable catalyst particle size in Fe(co)/SBA-15, the CNTs so produced tend to have a wide distribution of diameter (10-30 nm). In contrast, the CNTs produced

![Fig. 2. Low angle XRD patterns of (a) parent SBA-15, (b) Fe(co)/SBA-15, and (c) Fe(im)/SBA-15.](image)

![Fig. 3. TEM images of CNTs growth from Fe(im)/SBA-15 revealing that they are CNTs with (a) an averaged diameter of c.a. 7.7 nm and (b) closed ends.](image)
by using Fe(im)/SBA-15 appears to have uniform diameter of ca. 8 nm, which is comparable to the pore diameter of its parent SBA-15 support, as shown by the TEM image in Fig. 3a. A closer examination of the TEM image observed no Fe catalyst particle in the tips of these close-end type CNTs (Fig. 3b), suggesting that their formation follow the base growth mechanism route. The reasons for such preferred formation mechanism in the powdered substrate system is rather intriguing and deserves further investigation.

Finally, it is worth mentioning that the methodology and CVI procedure reported herein to fabricate CNTs with controllable sizes were also found to be unique in promoting the production yields. More specifically, a maximum CNTs yield of ca. 2.5 g/h was achieved for the supported Fe/SBA-15 catalysts in the present system design with a reactor chamber volume of ca. 30 mL. Taking the weight ratio of CNTs/carbon in C2H2 into account, it is estimated that ca. 78% of the C2H2 carbon source were efficiently transfer into CNTs. Thus, the methodology reported herein should be useful for industrial applications, particularly in quality control and mass production of CNTs.

4. CONCLUSIONS

By using mesoporous silica as template and catalyst support, we have demonstrated that high quality CNTs can be fabricated not only with superior yield but also with uniform diameters that can be tailored by the pore size of their template.

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