

**Single-walled carbon nanotubes catalytically grown from
mesoporous silica thin film**

Yoichi Murakami^a, Shigehiro Yamakita^b, Tatsuya Okubo^c, Shigeo Maruyama^{a*}

^a*Department of Mechanical Engineering, The University of Tokyo*

7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

^b*Department of Chemical System Engineering, The University of Tokyo*

7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

^c*Department of Chemical System Engineering, The University of Tokyo, and PRESTO, JST*

7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan

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Abstract

A new technique of synthesizing single-walled carbon nanotubes (SWNTs) from a thin film of SBA-16 type mesoporous silica (MPS) on a Si substrate was developed. The alcohol catalytic CVD method was employed for the low temperature synthesis of SWNTs to minimize the sintering of catalytic metals and damaging of the MPS structure. The role of MPS layer is discussed based on SEM and Raman analyses, in comparison with the reference experiments made using Si substrates coated with silica thin films. This technique suggests a possibility of synthesizing SWNTs at well-defined intervals utilizing the periodic structures of MPS.

*Corresponding Author. Fax: +81-3-5800-6983.

E-mail address: maruyama@photon.t.u-tokyo.ac.jp (S. Maruyama).

1. Introduction

Since the discovery [1], single-walled carbon nanotubes (SWNTs) have been an extensive research object in various scientific and industrial fields due to its unique properties and remarkable potentials as a new material. So far, several studies [2-5] have been reported to synthesize carbon nanotubes directly on silicon wafer as a preliminary step for incorporating them into electronic circuits. However, this approach has resulted in the occasional production of multi-walled nanotubes (MWNTs) [3-5] due to a sintering of deposited/sputtered catalytic metals, which can be caused by their higher CVD temperature (typically 900 °C) and almost perfect flatness of Si surface. From this concern, mesoporous silica (MPS) could be an ideal material for achieving well-regularized synthesis of carbon nanotubes with an expected effect of preventing sintering of catalytic metals.

To date, several attempts have been made to synthesize carbon nanotubes using MPS as a catalytic support [6-13]. Powders of various types of MPS were employed for mass production [6, 9, 10], but they all have resulted in MWNTs except Okamoto et al. [10], who synthesized some amount of SWNTs with MWNTs. Films of MPS were sometimes formed on solid substrates [7, 8, 11-13], but their major products were MWNTs and no successful synthesis of SWNTs has yet been reported. For instance, no evidence has been presented by Huang et al. [13] on whether the produced nanotubes are single-walled or multi-walled products.

We propose here a new methodology of synthesizing high-quality SWNTs employing a thin film of cubic type SBA-16 that has accessible pores on the surface. Our method of metal loading differs from any of the past reports [7, 8, 11-13], where the catalytic metal was pre-mixed in the stage of silica formation. SWNTs have been synthesized from MPS thin film on a Si substrate using the alcohol catalytic CVD method developed by our group [14, 15], by which we have been able to produce high-quality SWNTs at temperature as low as 550 °C.

2. Preparations and Experiments

A thin film of SBA-16 was coated on a Si substrate following Zhao et al. [16]. First, TEOS (tetra-ethyl-ortho-silicate), ethanol, H₂O, and HCl were mixed and stirred for 1 h at 65 °C to form a sol-gel solution. This solution was mixed with an ethanol solution of amphiphilic triblock copolymer [(C₂H₂O)₁₀₆ - (C₃H₄O)₇₀ - (C₂H₂O)₁₀₆] (BASF, F127) and stirred for another 2 h at room temperature. The self-assembled polymers served as a structure-directing agent (SDA) in the formation of mesopores. The overall composition of prepared mixture was fixed to {TEOS : H₂O : HCl : Ethanol : polymer = 1 : 9.2 : 0.021 : 40 : 7.2×10⁻³} in molar ratio. The solution thus prepared was mounted on a piece of Si substrate (2 cm × 2 cm) by the dip-coating method at a constant pull-up rate of 6 cm/min. After the coating, the piece was dried in air at 80 °C overnight and calcinated in air at 500 °C for 4 h to remove the polymers, by which an MPS thin film with a typical thickness of 50 nm was formed.

Subsequently, catalytic metal was loaded on the MPS-coated Si substrate (referred to as 'MPS/Si substrate'). Iron acetate (CH₃CO₂)₂Fe and cobalt acetate (CH₃CO₂)₂Co·4H₂O were dissolved in ethanol (typically 20 ml) to form a metal acetate solution so that the weight concentration of both metals were made equal, either 0.01 wt % or 0.001 wt % in this report. The MPS/Si piece was placed on the bottom of a beaker containing the metal acetate solution and was then transferred into a desiccator for evacuation by a rotary pump for 1 h. It is crucial to set the initial solution level below 10 mm to avoid sudden boiling during the evacuation. With this process, air remaining inside the mesoporous film was replaced with the solution. The piece's surface was washed immediately after drawn-out from the solution with ethanol by two different procedures, as described in a later section. The metal-loaded MPS/Si piece was heated up to about 400 °C in the

flow of He/O₂ (5 % O₂) to remove organic residues and to form oxidized bimetallic particles inside (or partly on the surface) of the thin film. As reference experiments, silica-coated Si substrates (referred to as ‘Silica/Si substrate’) without mesoporous structure were employed to examine the role of the mesopores. This Silica/Si piece was fabricated by identical procedures for the metal loading process but without addition of the polymers.

The subsequent CVD procedure was same as that presented in [15]. The reaction temperature, time, and ethanol vapor pressure employed in this study were 750 °C, 10 minutes, and 10 Torr, respectively. The gas used while heating up and cooling down of the electric furnace was Ar/H₂ (3 % H₂). Thereby synthesized SWNTs were characterized with FE-SEM observation (HITACHI, S-900) and Raman spectroscopic analysis (CHROMEX 501is and ANDOR DV401-FI for the spectrometer and CCD system, respectively). Laser wavelength of 488 nm was used for all Raman measurements.

3. Results and discussion

Figure 1(a) presents a SEM image of the MPS/Si surface before catalytic metal was loaded. Platinum film with a thickness of less than 0.5 nm (measured by a quartz crystal microbalance) was sputtered on the surface to enhance the visibility, and the observation was performed at 6 kV, where no charge-up occurred. The dark circular apertures correspond to the mesopores formed in the silica framework. The inset reveals that the mesopores were periodically located with an approximate interval of 15 nm. The pore size distribution of this MPS film was confirmed by the Barrett-Joyner-Halenda (BJH) analysis (Fig. 1(b)) using the MPS films coated on glass substrates in the N₂ absorption/desorption measurement. A sharp peak at 6 nm corresponds to the mesopores, and a less remarkable peak around 2.6 nm is ascribed to the diameter of connecting holes between the pores (see [17] for 3-D schematic of SBA-16).

Figure 2 shows SEM images of the MPS/Si surfaces after the CVD reaction with several magnifications. The metallic concentrations of the acetate solution used in Figs. 2(a) and (b) were 0.01wt% and 0.001 wt%, respectively. In both cases, the substrate surface was rinsed with ethanol immediately after the metal loading for about 3 s. The bright lines represent the bundles of SWNTs, which look somewhat blurred and thicker than actual: This is due to a change in the local emission property of secondary electrons, often observed for the SWNTs grown on Silica/Si surface [18]. The SWNTs in Fig. 2(a) look sparser and less uniform than those in Fig. 2(b). Notably, metal particles larger than 10 nm (bright dots) are densely inhabited on the MPS surface, where some of them seem to have sintered. These particles are seen to ‘clog’ the mesopores beneath them, which might be a partial reason for such sparser population of SWNTs.

In contrast, SWNTs shown in Fig. 2(b) look more densely and uniformly populated and very few metal particles are found on the surface. Then it is reasonably speculated that a certain amount of SWNTs were grown from inside of the MPS thin film. Another noticeable difference lies in the visibility of the surface: The surface structure is hardly recognizable in Fig. 2(a), while in Fig. 2(b) the fine structure of the MPS surface is clearly observed. Note that these two substrates were treated in the same batch in the processes of preparation, metal loading, CVD, and SEM observation. Usually, the surface of MPS cannot be observed without sputtering of metal particles, as exemplified in Fig. 1(a). This improved visibility was caused by a uniform coverage of its surface with SWNTs, which can act as an excellent conductor.

In order to examine the function of the MPS layer, SWNTs synthesized on the MPS/Si were compared with those on the Silica/Si substrate at a fixed metallic concentration of 0.001 wt%. Figure 3 presents Raman spectra of the SWNTs synthesized on the MPS/Si and Silica/Si substrates, and for each substrate two types of washing treatment were employed: The first method is that employed in Fig. 2, or a rinse of the surface with ethanol for about 3 s (denoted as ‘lightly rinsed’). The other method is a soak of the substrate into ethanol (typically 20 ml) for 10 minutes before it

was drawn out from the ethanol and dried in air (denoted as '10 min soaked'). In each case, spectra were measured at five different locations chosen randomly, and they were arithmetically averaged. All spectra were normalized by the height of the silicon-derived peak around 960 cm^{-1} . The interpretation of the Raman spectra of SWNTs is presented in the literature [19].

The right panel of Fig. 3 shows a high-frequency area, where the magnitude of the G-band around 1590 cm^{-1} relative to the Si peak at 960 cm^{-1} approximates the amount of synthesized SWNTs. When the 'lightly rinsed' washing treatment was employed, no significant difference in the G-band magnitude was observed between MPS/Si and Silica/Si cases. However, the difference became much clearer when they were treated with '10 min soaked' washing: No significant change in the G-band magnitude was observed in MPS/Si, while the magnitude in Silica/Si drastically decreased as expected. This indicates that the MPS layer serves as an efficient capacitor for catalytic metals, supporting our idea that many of SWNTs were grown from the metals inside of the mesopores.

A peak around 1350 cm^{-1} called the D-band represents the extent of disorder in the sp^2 arrangement of carbon atoms, from which the quality of SWNTs were estimated. Interestingly, in the case of MPS/Si the '10 min soaking' treatment has enhanced the quality of SWNTs. Furthermore, the standard deviation of the G-band intensities among the five measurements in the 'lightly rinsed' case was over 50 %, whereas that in the '10 min soaked' case was only 8 %, indicating that the soaking process has improved the uniformity of the catalytic distribution. As we speculate, the metals on the surface are also reduced through the '10 min soaked' process, but a more detailed analysis is essential for further discussion. The lower Raman spectra are magnified in the left panel of Fig. 3, presenting the radial breathing mode (RBM) peaks that identify SWNTs. The diameter distribution of SWNTs is estimated using ' $d\text{ (nm)} = 248 / \nu\text{ (cm}^{-1}\text{)}$ ' [20] where d is the SWNT diameter and ν is the Raman shift. The SWNTs synthesized on MPS/Si have diameters

around 0.9 ~ 1.5 nm.

Figure 4 shows SEM images of the above discussed MPS/Si substrate with '10 min soaked' treatment, taken from tilted angles so that their broken cross-sections can be included. The cross-section exhibits a three-layered structure of this MPS/Si substrate: The MPS top layer has an approximate thickness of 50 nm, and the SiO₂ layer with a thickness of 100 nm is seen below it. In the base is the Si substrate that looks darkened. The upper picture reveals that most of the SWNT bundles are adhered to the MPS surface to form a uniform, web-like network of SWNTs. The lower picture with larger magnification shows the fine structure of MPS beneath the SWNTs. No remarkable difference in the form of synthesized SWNTs from the case of 'Lightly rinsed' is observed in the FE-SEM observation. Some of the SWNT bundles are observed to detach from the surface, but they eventually collide with the surface again due to the flexibility of SWNTs and are captured by the van der Waals attraction of silica frameworks.

With further FE-SEM observation of the broken cross-section with higher magnification, we have occasionally observed metal particles embedded in the MPS layer from which SWNTs were extended. These images support our idea regarding the role of the MPS layer; however, they are not sufficiently convincing for a clearer discussion on the morphology of SWNTs and the metallic particles located inside or on the surface of the MPS layer. A further detailed study is needed for their characterization by the use of e.g. a cross-sectional HRTEM analysis [21].

4. Concluding remarks

High-quality SWNTs have been synthesized on SBA-16 type MPS thin film and its function has been elucidated through a reference experiment with Silica/Si substrate. The MPS layer provides an additional volumetric capacity for holding catalytic metals inside it, and a physical potential for prevention of sintering. The present CVD process at relatively low temperature contributes to the prevention of metallic sintering at the same time to the preservation

of the MPS structure. This study has suggested a possibility of growing SWNTs regularly in well-defined intervals by utilizing the periodic structure of MPS.

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Figure Captions

Fig.1. (a) SEM image of the platinum-sputtered MPS/Si surface before loading of catalytic metal. The dark apertures correspond to the mesopores formed in silica framework. (b) Pore size distribution of current MPS thin film calculated using the BJH analysis.

Fig. 2. SEM images of MPS/Si surface after the CVD reaction when the metallic concentration in the solution used in the metal loading process was (a) 0.01 wt% and (b) 0.001 wt%. The employed washing treatment was a light rinsing in ethanol. Horizontal lines denote 100 nm.

Fig. 3. Raman spectra of MPS/Si and Silica/Si substrates after the synthesis of SWNTs. The metallic concentration during the metal loading process was 0.001 wt% for all cases. For each substrate, two types of washing treatment noted in text were employed.

Fig. 4. SEM images of MPS/Si substrate after the synthesis of SWNTs taken from a tilted angle. The metallic concentration during the metal loading process was 0.001 wt%, and the substrate was subsequently soaked in ethanol for 10 min.

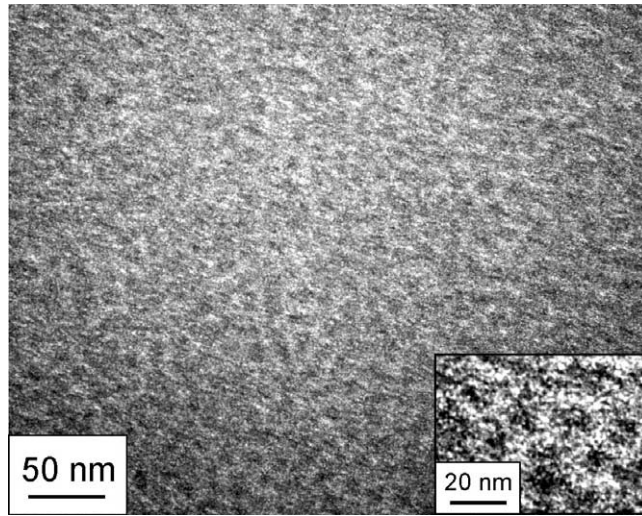


Fig. 1(a).

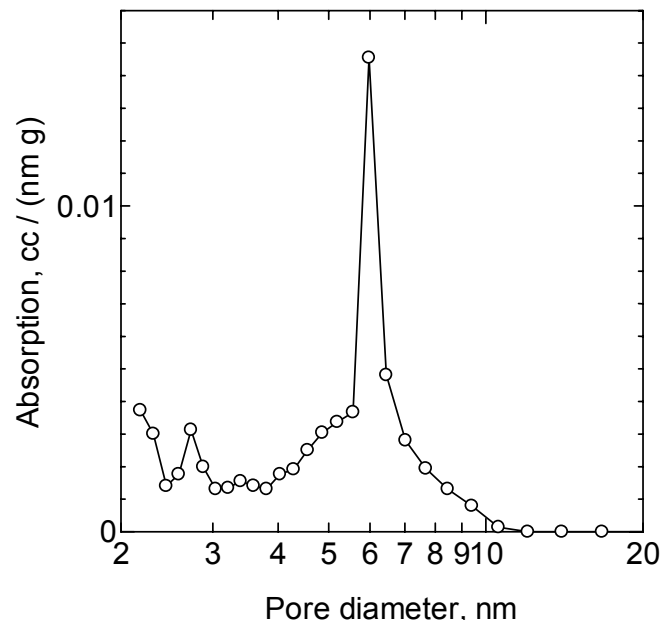
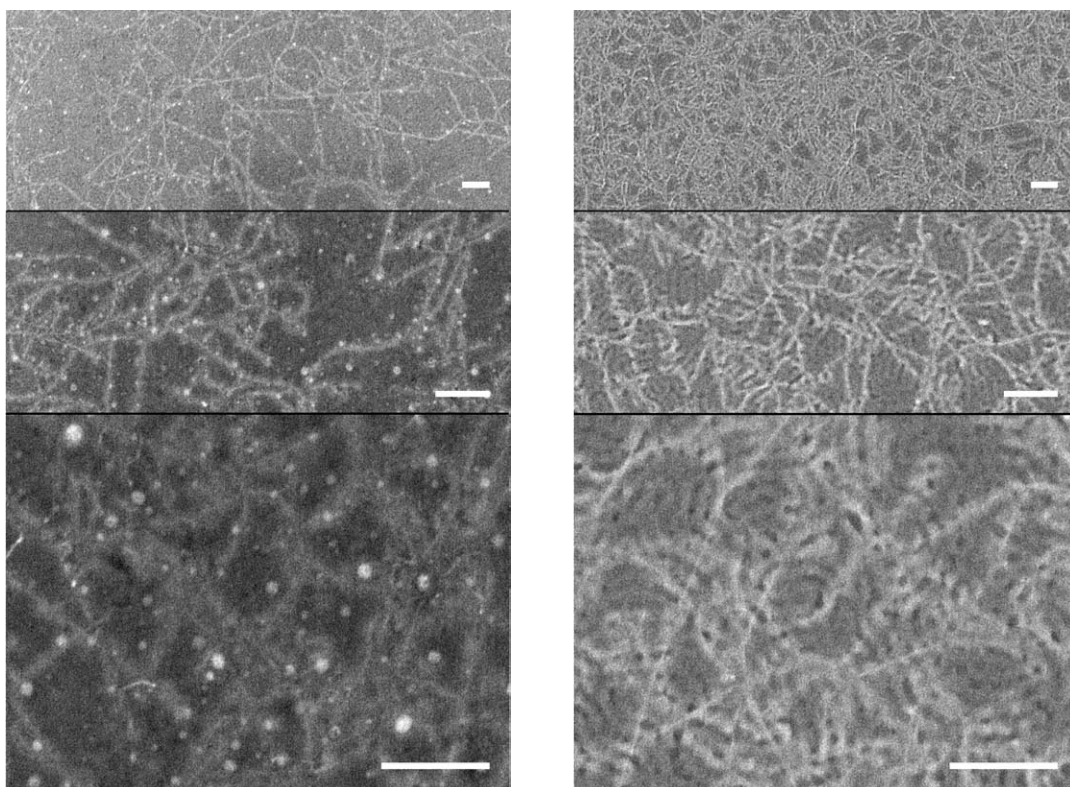


Fig. 1(b).



(a)

(b)

Fig. 2.

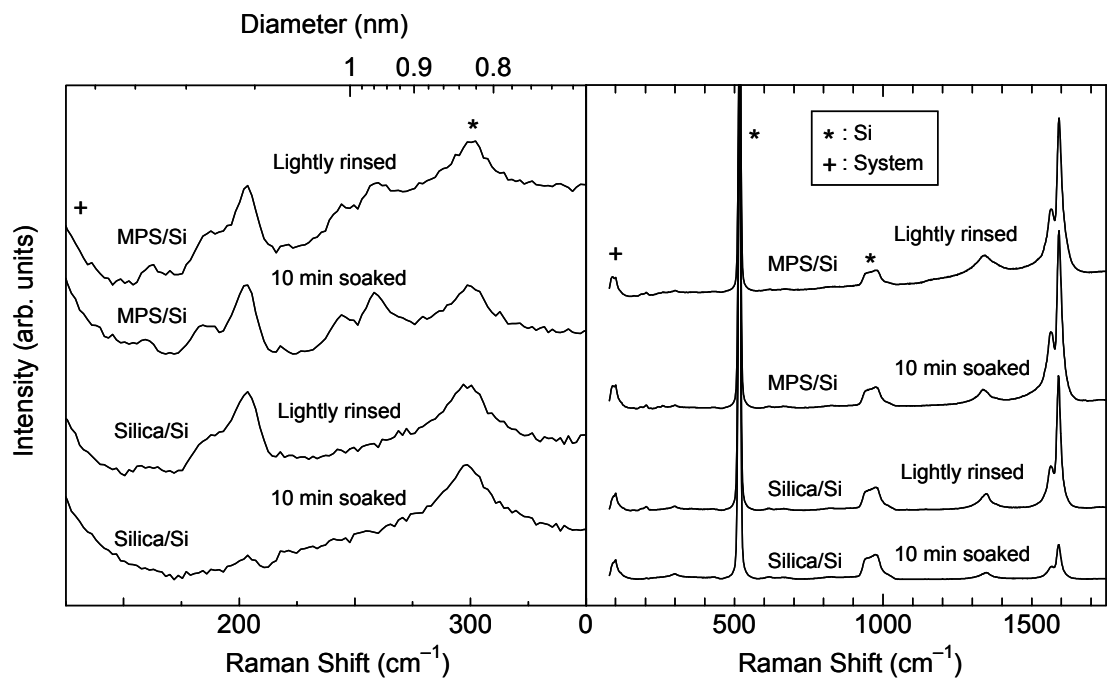


Fig. 3.

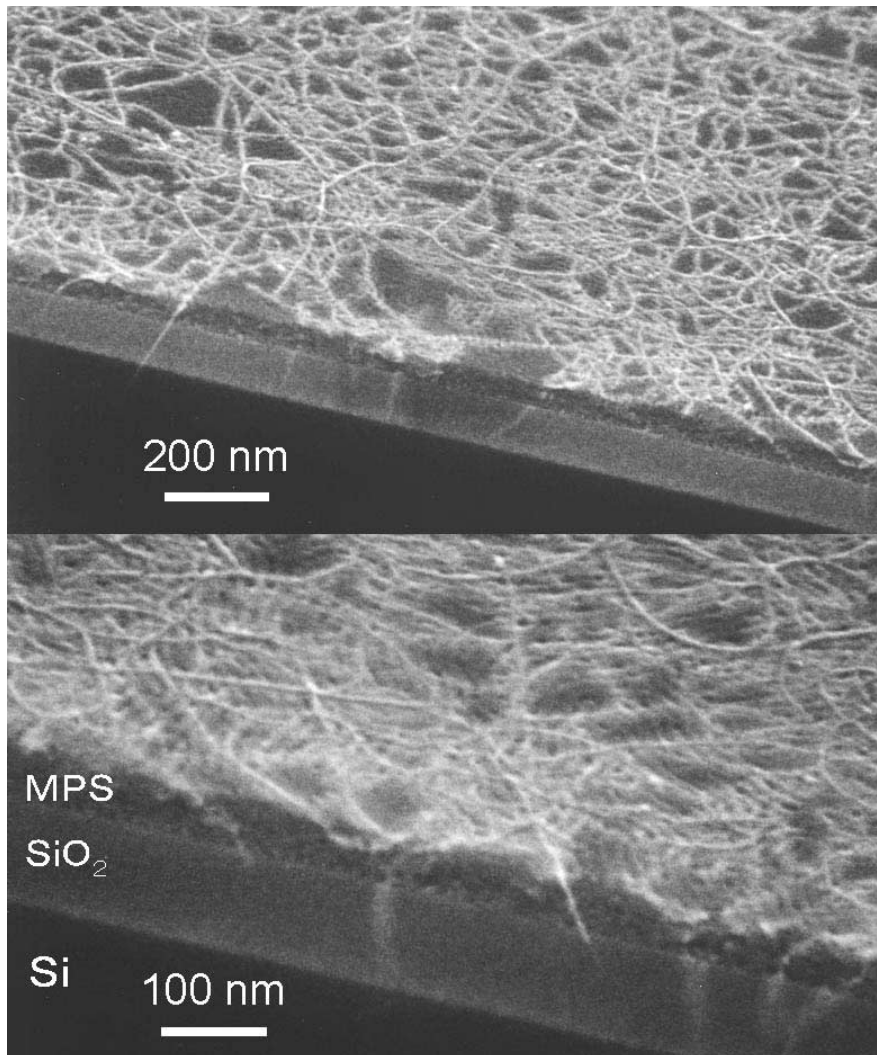


Fig. 4.