High-yield synthesis of thin multiwalled carbon nanotubes and their field emission characteristics

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Abstract

We have synthesized thin multi-walled carbon nanotubes (t-MWCNTs) using a catalytic chemical vapor deposition (CCVD) method with FeMoMgO catalyst. The number of tube walls were 2 ~ 6 with the corresponding diameters of 3 ~ 6 nm. We obtained high production yield of over 3000 wt% compared to the weight of the supplied catalyst. These t-MWCNTs revealed the intermediate structural characteristics between single- and multi-walled carbon nanotubes (SWCNTs and MWCNTs). We have also characterized the field emission properties such as turn-on field and emission current, and current degradation from these t-MWCNTs together with SWCNTs and MWCNTs.

1. Introduction

In addition to an early synthesis of SWCNTs and MWCNTs, the double-walled carbon nanotubes (DWCNTs) have been synthesized recently. Despite strong applicability of nanotubes, applications are still limited by their electronic and atomic structures. For example, large field enhancement factor, high conductivity, and high durability of emission tip are necessary for an efficient field emitter. SWCNTs have been reported to provide large field enhancement factor, low threshold voltage, and high emission currents [1], but the substantial degradation of emission currents have been shown to be a serious bottleneck for the application of SWCNTs-based field emission display (FED) [2]. In contrast with SWCNTs, MWCNTs have shown high emission stability but small field enhancement factor. DWCNTs could be an alternative for this purpose but the poor production rate and the redundant purification process have been a serious drawback.

2. Experimental

FeMoMgO catalysts were prepared by combustion synthesis [3]. Aqueous solution of iron nitrate, magnesium nitrate, and ammonium molybdate were mixed together. The citric acid as a foaming and combustion additive were added to it, followed by the mild sonication and stirring. The mixture was directly loaded into the furnace and fired at 550 °C for 5 min. The hydrogen gases were flowed to reduce the catalyst powder at 900 °C for 30 min. Thin MWCNTs were then synthesized at the same temperature with a gas mixture of hydrogen, methane, and ethylene under an atmospheric pressure. We have fabricated t-MWCNTs based-field emitters together with SWCNTs and MWCNTs on indium tin oxide (ITO) coated-glass substrate by spraying method and investigated their field emission characteristics.

3. Results and discussion

Fig. 1a shows the photo image of the FeMoMgO powder before reduction. The boat was overflowed with nanotubes when a methane gas was flowed for 30 min at 900 °C, as shown in Fig. 1b. The soot product was multiplied by about 1350 wt% compared to the originally reduced catalyst. Figs. 1c and 1d show the typical FESEM images of the as-grown t-MWCNTs. Nanotubes are usually long without the observable tube ends similar to SWCNTs. The bundle size seems to be rather narrow compared to those of SWCNTs and DWCNTs. Figs. 1e-1g show a series of images from HRTEM. Nanotubes are usually straight with rather small bundle sizes, as shown in Fig. 1e, in good agreement with the SEM images. Nanotubes are mostly clean without amorphous carbon particles on the tube walls. The diameters of the outer walls range from 3 nm to 6 nm. Some nanotubes have rather large inner diameter of 3 nm, as shown in Fig. 1f.

Fig. 2a demonstrates the distribution of the number of nanotube walls. The most probable number of walls is four. It is well known that the nanotube diameters are determined by the size of the catalyst.

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Our results suggest that the catalysts are very uniformly distributed over the MgO supporter, which is the main role for the metal oxide supporter, and consistent with the previous reports [4]. Fig. 2b shows the TG and differential TG of the as-grown sample in air atmosphere. The sample starts burning near 500 °C and ends burning near 650 °C. The remaining quantity is 6.8 ± 0.3 wt%, which is the mass of oxidized catalyst with MgO supporter.

Figs. 2c and 2d show the yield of nanotubes (mass of the total product/mass of the catalyst including MgO supporter after reduction) as a function of growth time and ethylene/methane flow rate ratio, respectively. In Fig. 2c, 90 wt% of nanotubes were produced during an early stage of 30 min with respect to the 120 min. The high yield of 1450 wt% nanotubes was obtained at two hours of growth time using the methane gases without ethylene gases. Ethylene gas is generally known to be less stable than methane gas. This means that ethylene gas can be easily decomposed at high growth temperature, and the decomposed carbon atoms increase enough with increasing the flow rate of ethylene gas, enhancing the nanotube yield. For this reason, we increased the flow rate of ethylene gas with respect to the methane, as shown in Fig. 2d. In this case, we fixed the growth time at 120 min. As the ethylene/methane ratio increases, the nanotube yield increases continuously. We emphasize here that the yield reaches 3050 wt% at an ethylene/methane ratio of 10 %. This is extremely high, compared to the previous reports of less than 280 wt% [5]. This high yield of t-MWCNTs is contributed from two factors: i) large number of available catalyst sites and ii) an efficient catalytic reactivity. In the FeMoMgO catalyst, the role of each species is different. The Fe catalysts are well distributed on MgO supporter and prevented from being aggregated together, which resulted in maintaining their small sizes during high temperature synthesis. The Mo particles act as a promoter to increase the nanotubes yield. In order to increase the catalytic reactivity, the reduction process of catalyst is an essential step. In our case, we achieved this by performing both reduction and the subsequent nanotube synthesis at the same chamber. This prohibits re-oxidation of catalysts such that highly efficient catalytic reactivity is maintained and at the same time all the reduced catalysts could be utilized for nanotube synthesis. In order to prove this, the catalyst reduction was done separately and brought into the growth chamber such that the re-oxidation takes place during transferring the catalyst. We found that the yield was dropped significantly, as shown in the open circles in Fig. 2d. On the other hand, because the saturation behavior did not occur at an ethylene/methane ratio of 10 %, the nanotube yield might be increased at larger ethylene/methane ratio. However, the co-products such as amorphous carbon particles and thick MWCNTs could be also obtained. Therefore, the high yield synthesis of the pure t-MWCNTs should be optimized with care.

Figures 3a and 3b show the current density-electric field (*J*-*E*) characteristics and corresponding Fowler-Nordheim (FN) plots of SWCNTs, t-MWCNTs, and MWCNTs based-field emitters, respectively. In Fig. 3b, the turn-on field of t-MWCNTs is lower than that of MWCNTs. This is attributed to the higher field enhancement factor of t-MWCNTs than that of MWCNTs. Actually, the field enhancement factor relates strongly to the aspect ratio of nanotubes [6]. As the aspect ratio increases, the field enhancement factor does as well, resulting in the low turn-on field and high current density. On the other hand, we can also observe that the turn-on field of t-MWCNTs is similar to that of SWCNTs. It can be ascribed to the less bundling effect of t-MWCNTs than SWCNTs, resulting in comparable field enhancement factor of t-MWCNTs to SWCNTs. In addition to this, we should note that t-MWCNTs have the higher current density under 3.5 V/μm than SWCNTs even though relatively lower field enhancement factor as shown in Fig. 3a. In fact, the screening effect which is arisen from the huge emitter density can reduce the emission currents. In this case, however, this unusual behavior cannot be explained by the screening effect due to the very similar emitter density and length of SWCNTs and t-MWCNTs. From the high field region of FN plots in Fig. 2(b), we can observe that the slope of SWCNTs changes and slightly increases. This means that SWCNTs have the lower chemical and physical stability than t-MWCNTs at high field region. For more detailed study, we investigated the emission stability of three nanotubes under the high field.

Figure 4a show the degradation rate of the emission current density (J/J_i) at the same electric field of 2.8 V/μm. The initial current density (J_i) of SWCNTs, t-MWCNTs, and MWCNTs is 0.17, 0.19, and 0.09 mA/cm^2, respectively. We can clearly observe that the emission current density of SWCNTs drastically decreases to 10 % after 12 hours. We also note that the current degradation rate of t-MWCNTs is similar

to that of MWCNTs, even though the initial current density of t-MWCNTs is higher than that of MWCNTs. Therefore, we can conclude that the stable emission of t-MWCNTs is attributed to their chemical and physical stability similar to MWCNTs. The photo image of emission pattern from t-MWCNTs with a size of 1 x 1 cm^2 is shown in Fig. 4b. We got the uniform and extremely bright electron emission from t-MWCNTs using phosphor coated-ITO glass as an anode. This plane-type field emission, not a spot-type, is attributed to the uniform length, diameter, and density of t-MWCNTs emitters in whole area.

3. Conclusion

We have demonstrated very high yield synthesis method of t-MWCNTs using CCVD with a FeMoMgO catalyst. Large number of available catalyst sites and an efficient catalytic reactivity are two crucial factors to control. The catalytic reactivity was maximized by performing the reduction of catalyst and consecutive synthesis of nanotubes in the same chamber. We also found that t-MWCNTs have the higher current density and lower turn-on field than MWCNTs due to the higher field enhancement factor. It was also observed that the current degradation rate of t-MWCNTs was very similar to that of MWCNTs, but SWCNTs decreased drastically their currents during 12 hours. This stable emission of t-MWCNTs might result from their chemical and physical stability similar to MWCNTs. Therefore, t-MWCNTs could be a good field emitter for FEDs.

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5. References

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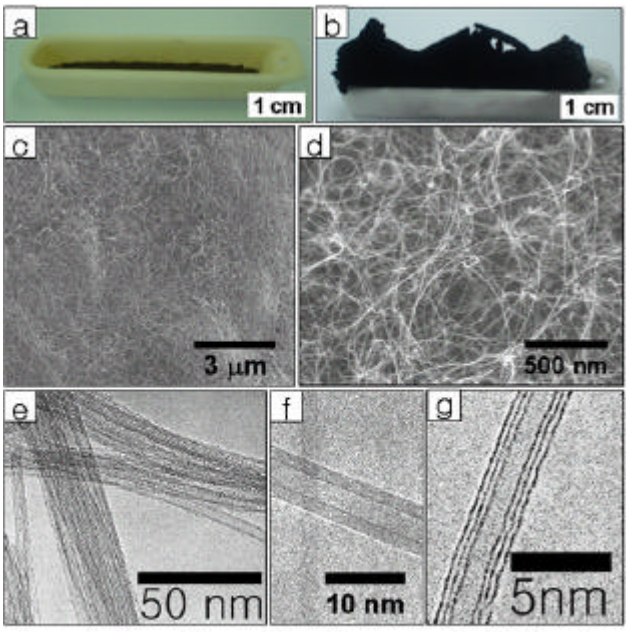

Figure 1. Photo images of the ceramic boat with FeMoMgO catalyst (a) before and (b) after the nanotube synthesis. (c), (d) FESEM images and (e)–(g) HRTEM images of as-grown carbon nanotubes.

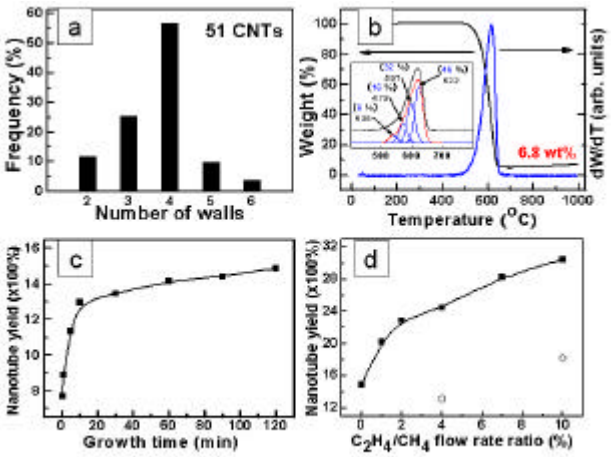

Figure 2. (a) Distribution of the number of nanotube walls measured from TEM observations and (b) TG and DTG of as-grown carbon nanotubes. The nanotube yield in terms of (c) the growth time and (d) the ratio of flow rate of ethylene and methane gases.

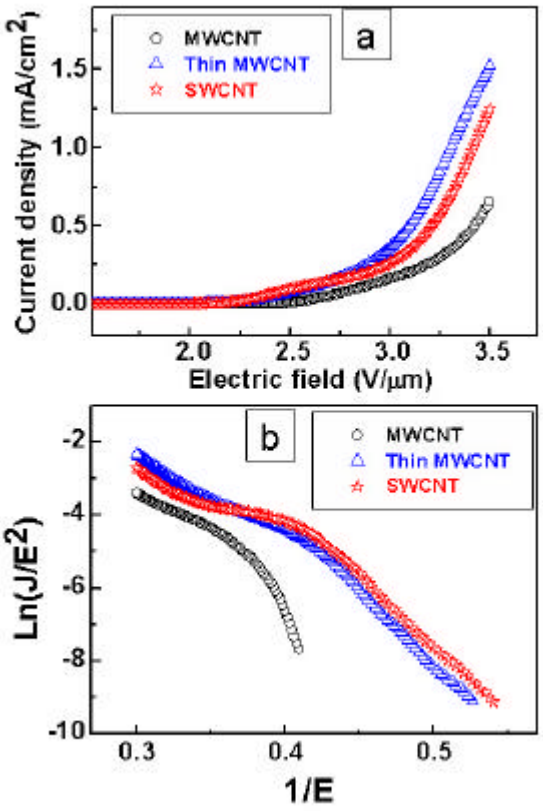

Figure 3. (a) *J-E* characteristics and (b) their FN plots of SWCNTs, t-MWCNTs, and MWCNTs based-field emitters.

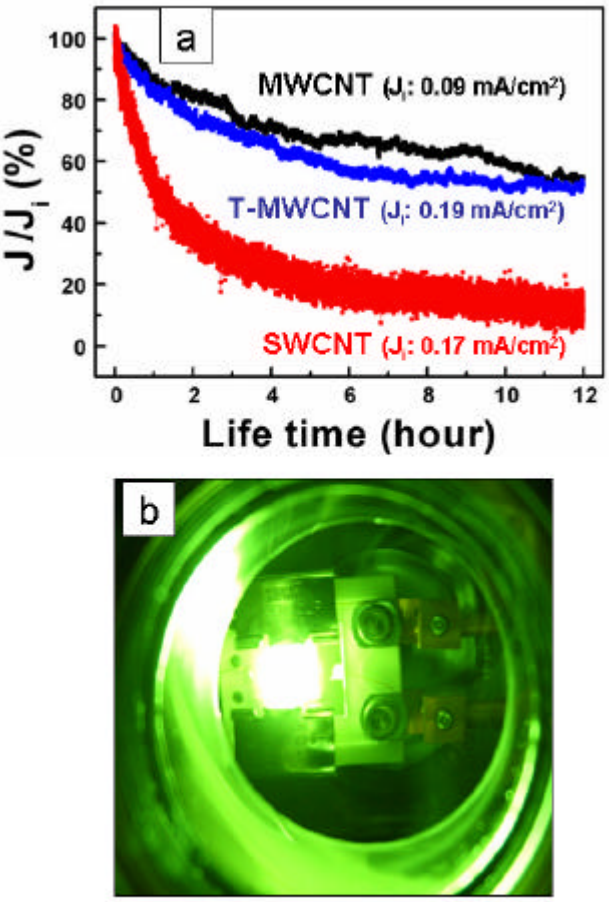

Figure 4. (a) Emission current stability of SWCNTs, t-MWCNTs, and MWCNTs based-field emitters for 12 hours at same electric field of 2.8 V/mm. (b) Photo image of emission pattern for t-MWCNTs based-field emitters with a size of 1 x 1 cm2.