Research Letter

Preparation of Powdery Carbon Nanotwist and Application to Printed Field Emitter

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In the present study, an automatic production system with sequencer control for the synthesis of carbon nanofibriform based on catalytic CVD using a substrate was developed. The carbon nanotwist (CNTw), which is one of the helical carbon nanofibers, was then synthesized in powdery form with an Ni-SnO₂-composed catalyst. The production rate was 5 400 times that of the conventional CVD system and Ni-Cu-In₂O₃ catalyst. The powdery CNTw was easily scraped off the substrate, then pasted with organic binder, and printed by a squeegee method on ITO glass substrate for an electron field emitter. The field emission performance was found to be better than that of the directly grown CNTw film in conventional CVD with Ni-Cu catalyst.

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1. INTRODUCTION

Some carbon nanomaterials are considered to be attractive and potential materials for an electron field emitter in next-generation flat panel displays [1]. Fibriform carbon nanomaterials, such as carbon nanotube (CNT) and carbon nanofiber (CNF), are synthesized by an arc discharge method and various types of catalytic chemical vapor deposition (catalytic CVD). There are two approaches to prepare the field emission cathode using carbon nanomaterials for a field emission display (FED) or device: one is direct film-growth deposition on a substrate by CVD, and the other is application of the presynthesized carbon nanomaterials on a substrate by various methods such as spin coating, dip coating, spray deposition, and print. The most cost-effective method is considered to be a printing method, which is currently used in the industrial manufacturing process of vacuum fluorescent display (VFD).

Helical carbon nanofiber (HCNF), which is a carbon nanofiber with helix shape and is 50 to 500 nm in fiber diameter, is one of the candidates for field emitter material, and its

potential has been demonstrated [2]. HCNFs are categorized into carbon nanocoil (CNC), carbon nanotwist (CNTw), and carbon nanorope (CNR) [3]. The CNC has a spring-like shape with a hollow along its outward form, whereas CNTw has a twisted string-shape without such a hollow. The CNR has a shape with multistrings twisted together. The HCNF has been synthesized and studied since the 1970s [4–15]. The CNC and CNTw relatively have good reproducibility, but CNR has been seldom seen. So far, various catalysts have been tried. For example, for CNC, Ni [4], Fe-ITO [8], Cu-(Ni, Cr, Ti or Zn) [9], Au [10], Fe-SnO₂ [11, 12], and Fe-based alloys (Fe-Cr-Mn-Mo, Fe-Cr-Ni-Mo (SUS513)) [13] have been tried, while for CNTw, Ni [4], Ni-Cu [3], Cu [14], and Fe-based alloys (Fe-Ni-Cr-Mo-Mn-Sn) [15] have been used. Compared with CNC, the CNTw has been able to be prepared in almost 100% purity with high uniformity of fiber diameter and shape [3]. However, only the thin-film form of CNTw has been obtained on the substrate [3] and not in sufficient amounts to apply to the printing method to prepare FED. A large amount of CNF in powdery form can be synthesized by the catalyst injection CVD method, but not for

TABLE 1: CVD conditions for direct film-growth and powdery synthesis of CNTw.

Process conditions	Conventional CVD	Automatic CVD
Reactor tube inner-diameter	40 mm	94 mm
Catalyst	Ni-Cu-In ₂ O ₃	Ni-SnO ₂
Source gas	C ₂ H ₂ (80 sccm)	C ₂ H ₂ (350 sccm)
Dilute gas	He (420 sccm)	N ₂ (1400 sccm)
Temperature	470°C	650°C
Process time for 1 substrate	30 min	10 min

HCNF, which has been prepared only in the CVD method with substrate, so far.

In the present study, an automatic CVD system with consecutive substrate transfer mechanism was developed in order to prepare a sufficient amount of HCNF. Then, a powdery form of CNTw on the substrate was obtained by employing a different catalyst from the usual one. The powdery CNTw was pasted and the FED was prepared by the squeegee printing method. The field emission property of the printed CNTw cathode was measured in comparison with the direct film-growth of CNTw.

2. EXPERIMENT

2.1. Direct film-growth of carbon nanotwist

CNTw film was directly grown and deposited on Ti-coated glass in the conventional CVD reactor reported previously [3]. A CVD electric furnace with horizontally-arranged quartz tube was used. The diameter of the quartz tube was 40 mm and the uniform temperature region of the furnace was approximately 200 mm. Ti thin film (approximately 200 nm thickness) was coated on the whole surface of a quartz-glass substrate (20 mm × 25 mm, 1 mm thick) at room temperature by cathodic vacuum arc deposition in order to make the electrical lead and to avoid the peeloff of the CNTw film. The catalytic liquid containing Ni, Cu, and In₂O₃ was applied on an 18 mm × 23 mm area of Ti-coated glass substrate with a spin coater. The CVD condition was summarized in Table 1.

2.2. Preparation of powdery carbon nanotwist

The newly developed CVD system was depicted in Figure 1. The system was composed of substrate loading chamber, transfer chamber, process reactor with electric furnace, and cooling chamber. Two gate valves separated the loading, transfer, and cooling chambers. No separation existed between the transfer chamber and the process reactor. All chambers were made by stainless steel, except a horizontally placed process reactor (quartz tube, 94 mm inner diameter). A substrate cassette containing up to 8 substrates 70 mm in diameter at the same time was placed in the loading chamber. Each substrate was then transferred from the cassette to the process reactor by the cassette-elevator robot-arm, horizontal robot-arm, and vertical robot-arm. After the reaction, the substrate was transferred to the cooling stage in the cool-

- (a) Reactor quartz tube (94 i.d.)
- (b) Substrate (70 o.d.)
- (c) Electric furnace
- (d) Gate valve
- (e) Loading chamber
- (f) Transfer chamber
- (g) Cooling chamber
- (h) Substrate cassette
- (i) Collection pot
- (j) Horizontal robot-arm
- (k) Vertical robot-arm
- (l) Cassette elevator robot-arm
- (m) Rotary actuator

FIGURE 1: Schematic diagram of automatic CVD system with consecutive substrate transfer mechanism.

ing chamber. The cooling stage had a rotary actuator, and the substrate was dropped to the bottom of the collection pot after sufficient cooling. This procedure was controlled by a sequencer, and the substrates were one by one transferred and treated while keeping the furnace temperature in the process condition.

The CNTw in powdery form was prepared by the automatic CVD system. The substrate was graphite (70 mm in diameter, 2.5 mm thick). The catalytic liquid of Ni-SnO₂ was dropped on the substrate with a pipette, and the substrate was baked together with the catalyst at 400°C for 10 minutes in air before setting in the substrate cassette. The CVD conditions were summarized in Table 1.

2.3. Preparation of printed CNTw field emitter and measurement

The CNTw paste was prepared by hand mixing powdery CNTw with the organic binder (composed of ethyl cellulose and terpineol) for 30 minutes in a crucible. The pasted CNTw was printed on ITO-coated soda-lime glass substrate (30 mm × 30 mm, 1 mm thick) in the area of 20 mm × 15 mm by the

FIGURE 2: Photograph and micrograph of CNTw. (a) Direct film-growth of CNTw on Ti-coated glass substrate. (b) Powdery CNTw synthesized in automatic CVD system on graphite substrate. (c) Printed CNTw film on ITO glass substrate. Upper left, overall view; upper right, high-magnification SEM; lower, low-magnification SEM, respectively.

squeegee method. Mending tape (3M, CM-12; 35 μm thick) was used for a step mask. The printed CNTw was then dried at 120°C for 2 hours and baked at 400°C for 1 hour [16]. The thickness of the printed powdery-CNTw film after baking was approximately 5 μm, and the maximum thickness was approximately 30 μm. Although double and triple tapings (70 and 105 μm thick) were tried for a step mask, the thicker CNTw films peeled off from the substrate due to increased internal stress of the film.

The field emission property was examined in the vacuum chamber. The phosphor (ZnO:Zn) anode thickness was approximately 15 μm. The anode diameters were 5 mm and 4 mm and the gap lengths were 50 μm and 100 μm for the cathodes of the direct film-growth CNTw and the printed CNTw film, respectively. The field emission experiment was carried out at 10^{-5} to 10^{-6} Pa.

3. RESULTS AND DISCUSSION

The synthesized and prepared materials were observed by a compact digital camera and by a scanning electron microscope (SEM; Hitachi, S-4500II). The results are shown in Figure 2.

In case of the direct film-growth CNTw, the CNTw yield in carbonaceous product was almost 100%, as shown in the SEM micrograph of Figure 2(a), and no other shape of car-

bonaceous material was found. The overview morphology of the film was quite uniform. The weight of the catalyst coated on the substrate was 0.7 mg. The film thickness was approximately 4 μm for 30-minute process time. These results indicated that the print method using the direct film-growth CNTw after removing from the substrate was difficult to apply, since the CNTw was insufficient. The weight of the film was 1.3 mg, evaluated from the weight change of the substrate before and after CNTw growth. Thus, the synthesis ratio of CNTw against the catalyst in weight, indicating the production efficiency on catalyst, was approximately 1.9, and the production rate was approximately 0.5 mg/h.

After various experiments to search the superior catalyst which has a higher reaction ability to grow CNTw, the catalyst of Ni-SnO₂ system was found to be excellent. Using this new catalytic system and automatic CVD system, CNTw was synthesized. As shown in Figure 2(b), the product of CNTw formed a softly-swollen dome shape on the substrate. So far, when 8 substrates were consecutively processed, approximately 6 g of CNTw was produced in 3 hours. In average, 900 mg CNTw was produced on 1 substrate by 36 mg of catalyst. Thus, the production rate was approximately 2,700 mg/h, and productivity of powdery CNTw was 5,400 times, compared with direct film-growth. The grown CNTw was easily scraped off the substrate and the powdery-form CNTw was obtained. Yield of CNTw shape material in

FIGURE 3: Field emission characteristics of CNTw films.

the carbonaceous product was almost 100%. The synthesis ratio of CNTw against the catalyst in weight was approximately 25. The fiber diameter of powdery CNTw was found to be thinner (average 90 nm) than that of the direct film-growth CNTw (average 150 nm).

Figure 2(c) shows the printed CNTw film using powdery CNTw. The film surface was quite rough with several aggregations, compared with the direct film-growth CNTw. Current-voltage characteristics indicating the field emission ability is presented in Figure 3. It was confirmed that the printed CNTw film has field-emission ability. Although the anode area was smaller and the gap space was longer, the printed CNTw film has a lower riseup voltage and larger current, compared with the direct film-growth CNTw. The adhesion of the printed CNTw film to the ITO substrate was not strong enough so the film was peeled off from the substrate by the electric field in case of 50-μm gap space. Moreover, the surface morphology was very rough due to many large aggregations and thus there were only a few electron-emission sites on the CNTw cathode in relation to the anode area. If the 50-μm gap assembly and macroscopically smoother surface morphology can be realized, the lower riseup voltage due to the higher electric field and the higher emission current due to the whole area emission or high-density electron-emission sites will be achieved. Therefore, in the next step, we must improve adhesion to the substrate and develop a new technique to control the surface morphology on the macro- and microscopic order to realize better performance by the CNTw field emitter.

4. CONCLUSION

Using an automatic CVD system and a newly found catalyst, CNTw was synthesized with a higher production rate

by the substrate method. The CNTw production rate increased to 2.7 g/h from 0.5 mg/h in the previous method. The powdery-form CNTw was obtained by scraping off the dome-like product from the substrate. Powdery CNTw could thus be used to prepare the CNTw paste and the CNTw film as the cathode of the field emitter was printed by the squeegee method. The field emission performance of the printed CNTw was found to be better than that of the direct film-growth CNTw. However, the performance was not superior to that of the carbon nanotube (CNT) emitter. Further improvement is required to develop a CNTw field emitter with higher performance and low-cost manufacture.

In addition, powdery CNTw is considered to allow CNTw application not only to field emitters, but also to products in various fields including conductive or reinforcement fillers, electrodes of chemical energy devices (fuel cells, secondary batteries, and supercapacitors), and templates for DNA handling.

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