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Preparation of a Highly Crystalline Single-Walled Carbon Nanotube Ink for the Synthesis of a Planar Field Electron Emitter

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Abstract

We synthesised a planar field emission (FE) cathode using a homogeneous dispersion of highly crystalline single-walled carbon nanotubes (HC-SWCNTs). We carried out a controlled dispersion to minimise crystal defects. Commercial SWCNTs were annealed under vacuum at high temperature to achieve a high degree of crystallinity. The HC-SWCNTs were then dispersed in an organic tin-doped indium oxide solution and characterised by transition electron microscopy, dTG, and UV-vis analyses. The FE cathode was prepared by coating the HC-SWCNT dispersion on a Si wafer and then physically carving the coated layer to expose the SWCNTs. As the results of some dispersion experiments, the crystallinity of HC-SWCNTs did not deteriorate in the dispersion process. The observed relationship between crystallinity and concentration of HC-SWCNT dispersions prepared using a wet-jet milling process suggested that the degree of crystallinity could be controlled. We achieved a HC-SWCNT dispersion concentration of more than 90 wt% whilst maintaining an extraordinarily high degree of crystallinity, which dispersion energy was higher than the cohesive energy depending on the high-order structure of the HC-SWCNTs. The FE area calculated from the Fowler-Nordheim (FN) -plots was found to be proportional to the HC-SWCNTs dispersion concentration.

INTRODUCTION

SWCNTs are known to exhibit excellent properties suitable for many applications because of a nanoscale needle shape [1], including chemical stability, thermal conductivity, and mechanical strength [2-5]. Field electron emitters are one of the most interesting applications for SWCNTs [6-13]; however, commercial SWCNTs contain many crystal defects and long emission stabilities cannot be obtained with these materials [6, 14]. Recently, Shimoi et al. reported that excellent emission properties, with an extraordinary emission stability of over 5000 h, were obtained by controlling the addition density of HC-SWCNTs up to about 0.7 mg/cm^2 in a planar emitter during preparation by a wet dispersion process [15]. However, the wet dispersion process resulted in a deterioration of the SWCNT crystallinity; it is difficult to disperse isolated SWCNTs in solution without including defects due to the strong cohesion force of about 100 MPa that exists between individual SWCNTs [16]. Therefore, it is important to confirm the extent of SWCNT crystallinity deterioration during wet dispersion processes.

The purpose of this study was to clarify the relationship between the crystallinity and dispersibility of SWCNTs to prepare a homogeneous and highly crystallised SWCNT ink for construction of a planar field emitter.

EXPERIMENTAL

Commercial SWCNTs (Meijo Nano Carbon, arc SO) were annealed under vacuum at 1300 K to prepare highly-crystalline SWCNTs. The highly-crystalline SWCNTs (HC-SWCNTs) were then dispersed in butyl-acetate containing an organic tin-doped indium oxide (ITO) precursor solution (Kojundo Chemical Laboratory, ITO-05C) as a conductive matrix and ethyl-cellulose (Wako, abt. 49 %-ethoxy 100 cP) as a dispersant. The mixing weight ratio of the HC-SWCNTs:ITO:ethyl-cellulose was 1:1200:24. HC-SWCNT-aggregate bundles were dispersed by either ultra-sonication at 40 kHz for up to 10 h or wet-jet milling (WJM; Sugino machine, Star Burst Mini) at 60 and 120 MPa for a maximum of 10 cycles. The mixture was then separated to a supernatant solution and others with a gravitational acceleration condition of 3600 G by a centrifuge to produce the final HC-SWCNT ink for use in field emitter preparation.

The field emission cathode was prepared by electrostatically layering the HC-SWCNT ink on a Si wafer to an expected density of 0.1 mg/cm^2 and then baking at 450 °C under vacuum (10^{-1} Pa). The cathode was then activated as a field emitter by physically carving the coated layer with many nicks to expose the HC-SWCNTs; each nick was 10 µm wide and separated from the other nicks by 100 µm.

The crystallinity and dispersibility of the HC-SWCNTs were quantified by transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and ultraviolet–visible (UV-vis) spectroscopy. The field emission properties of the cathode were determined from current–voltage (I-V) measurements using the system schematically depicted in Figure 1.

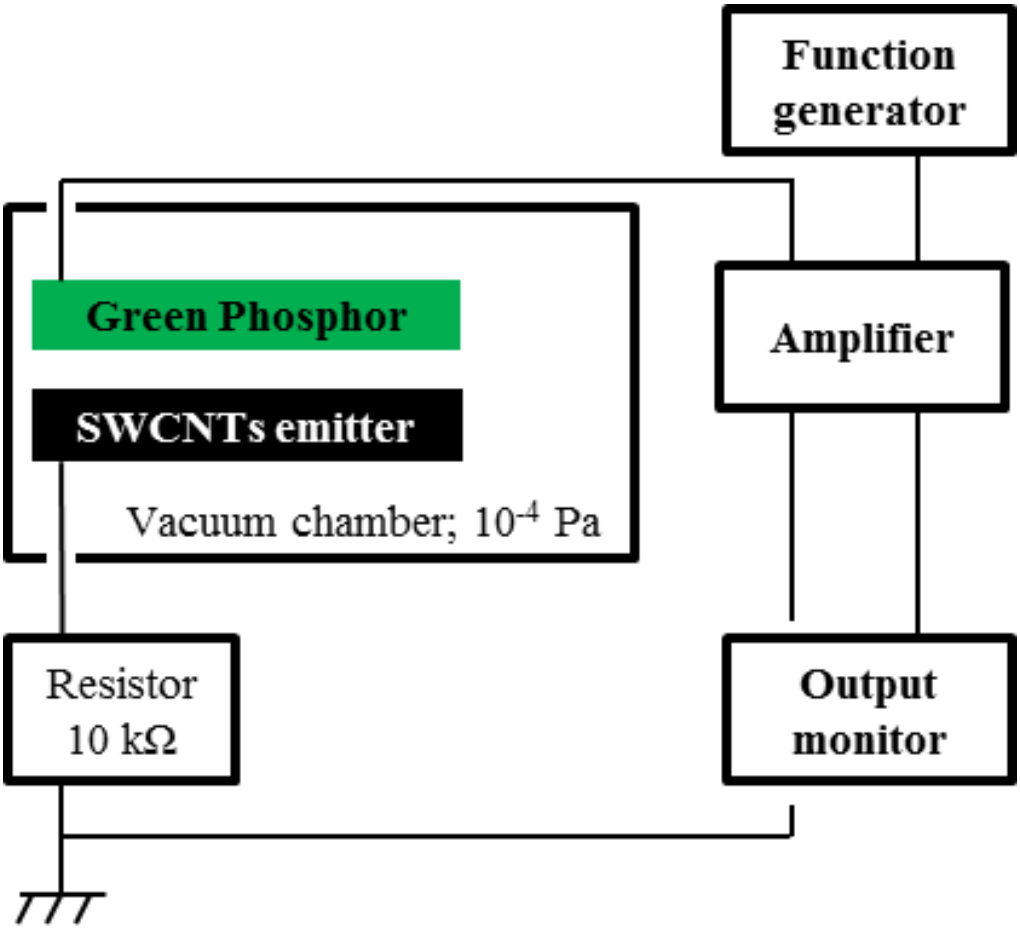

Figure 1. Schematic diagram of the current–voltage measurement system. A pulse wave with a duty cycle of 4 % at a frequency of 60 Hz was applied.

RESULTS AND DISCUSSION

Transition electron micrograph of the annealed SWCNTs is shown in Figure 2; only carbon nanotubes can be seen in the micrographs, with no other carbon contamination present. TG first derivative (dTG) curves for both SWCNT samples are shown in Figure 3 and indicate the weight fraction of tubes at each burning temperature. It is generally known that the burning temperature of SWCNTs is inversely proportional to the amount of crystal defects in the SWCNTs; hence, the SWCNT crystallinity can be inferred from the shape of the dTG curves. There are a few peaks in the commercial-SWCNT dTG curve, indicating a range of different crystallinities, and the burning temperature of the commercial SWCNTs increased after annealing, indicating an increase in the degree of crystallinity of the SWCNTs. However, the annealed-SWCNT dTG curve also indicated the presence of some lower crystallinity tubes that might deteriorate the field-emission stability.

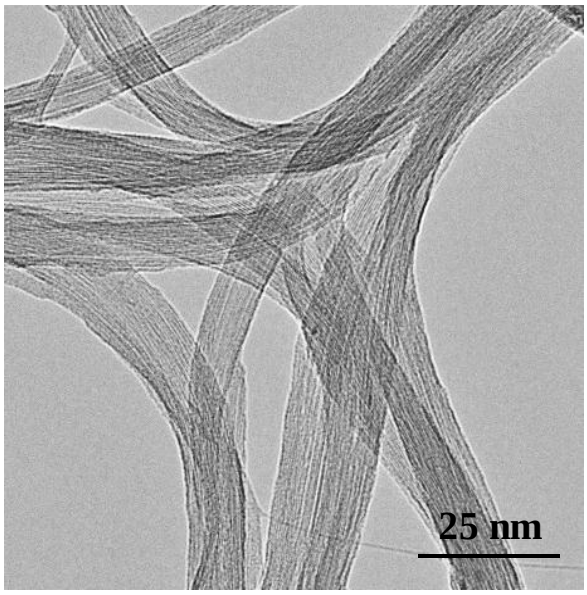

Figure 2. Transition electron micrograph of the annealed single-walled carbon nanotubes.

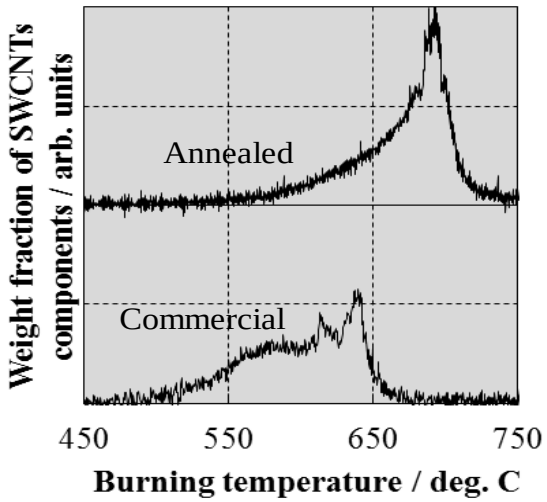

Figure 3. First derivative thermogravimetric curves of the commercial and annealed single-walled carbon nanotubes measured under an air atmosphere.

The relationship between dispersion concentration and crystallinity retention rate for HC-SWCNT dispersions prepared by ultra-sonication and wet-jet milling processes is shown in Figure 4. The dispersion concentration in Figure 4 was calculated from the ratio of dispersion transparency before and after centrifugation of the solution, as determined by UV-vis measurements, and includes HC-SWCNT aggregates. The crystallinity retention was calculated from the dot product of dTG measurement curves obtained before and after dispersion of the HC-SWCNTs and is presented as cosθ. A reduction in cosθ correlates to a deterioration in the crystallinity of the dispersed HC-SWCNTs. Thus, Figure 4 indicates that the HC-SWCNT crystallinity deteriorates with increasing sonication time; we propose that this is an effect of the uncontrollable cavitation that occurs during ultra-sonication. WJM was the most successful method for HC-SWCNT dispersion, with a concentration of more than 90 wt% and minimal crystallinity deterioration achieved. However, it should be noted that the crystallinity of the dispersed HC-SWCNTs also deteriorates with repeated milling and at higher operation pressures. It is considered to be difference of atom binding energy and cohesion energy depending on higher-order structure of SWCNTs [1, 15].

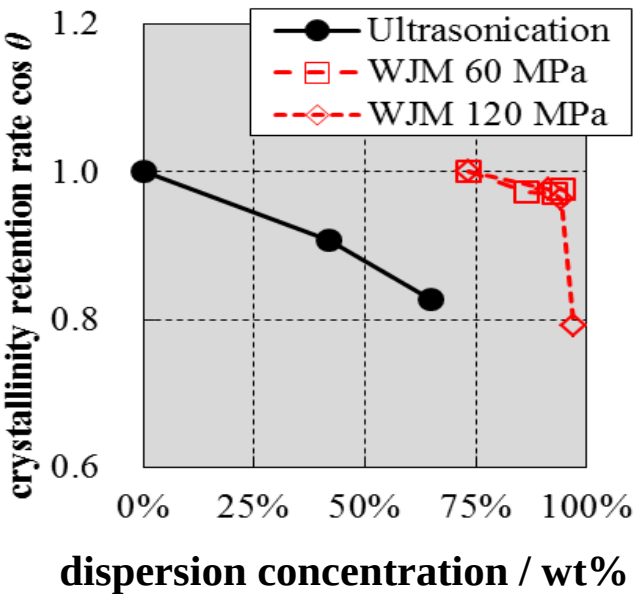

Figure 4. Dispersion concentration vs. crystallinity retention rate for highly crystalline single-walled carbon nanotubes dispersed by ultra-sonication and wet-jet milling. Ultra-sonication at 40 kHz was performed for 0, 5 and 10 h. Wet-jet milling was operated at both 60 and 120 MPa and repeated 1, 3, 5 and 10 times.

Figure 5 shows the current density as a function of field intensity for field emission cathodes prepared from HC-SWCNT inks dispersed by 1-10 WJM cycles at 120 MPa, and Table 1 shows the field emission properties calculated from Fowler–Nordheim plots converted using I-V plots and a work function value of 4.7 eV for SWCNTs [15,17-19]. The inset image in Figure 5 shows that a good planar lighting morphology was achieved using the homogeneously dispersed HC-SWCNT ink. The number of SWCNT field emission sites determines the homogeneity of the planar field emission, and the number of emission sites is proportional to the SWCNT dispersion concentration. We propose that the dispersed HC-SWCNTs contribute effectively to the field emission.

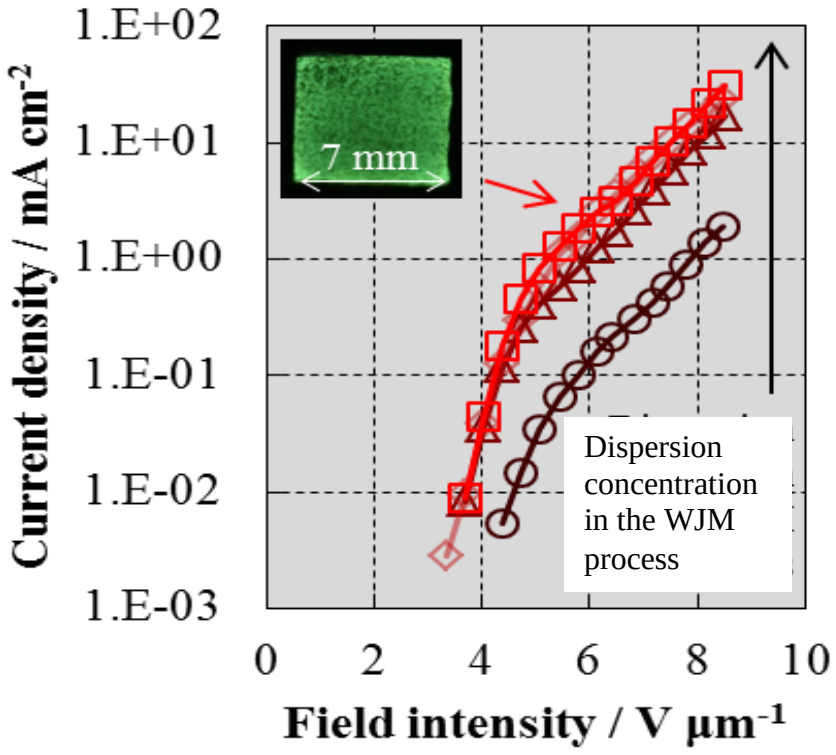

Figure 5. I-V plots of field emitters prepared using highly crystalline single-walled carbon nanotube inks dispersed by 1-10 wet-jet milling cycles at 120 MPa. The inset shows a luminescence photogram of 5 wet-jet milling cycles.

Table 1. Emission properties of field emitters prepared from wet-jet-milling dispersed single-walled carbon nanotube inks. Properties were calculated from Figure 6 using the Fowler-Nordheim-type electron tunnelling equation [11, 13-15].

WJM MPa	cycles	dispersion concentration	cos θ	emission site area	enhancement factor
120	1	73%	1.00	2.0E-16	7.0E+05
	3	91%	0.98	9.0E-16	7.0E+05
	5	94%	0.96	4.0E-15	6.0E+05
	10	97%	0.79	3.0E-15	7.0E+05

Figure 6 shows field emission stability curves for devices prepared from both the commercial- and HC-SWCNT inks dispersed by WJM at 120 MPa for 5 cycles. The HC-SWCNT-emitter current density is constant over more than 200 h after an initial decrease over the first 50 h. We attribute the initial decrease in current density to the lower-crystallinity HC-SWCNT phases in the emitter.

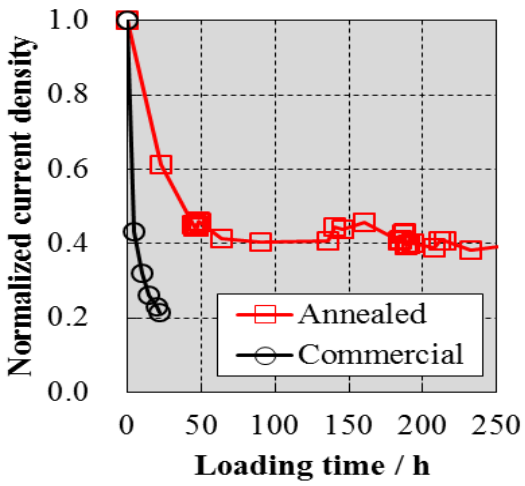

Figure 6. Field emission stability of highly crystalline single-walled carbon nanotube and commercial single-walled carbon nanotube emitters measured at 7 V/µm. Both emitters used SWCNT inks that were prepared by wet-jet milling at 120 MPa for 5 cycles.

CONCLUSION

We constructed a planar field-emitter cathode using a well-dispersed HC-SWCNT ink prepared by wet-jet milling. The degradation of HC-SWCNT crystallinity during the dispersion process was investigated by measurement of the resultant field-emission stability. We showed that high-crystallinity SWCNT dispersions could be prepared using wet-jet milling, and the initial emission stability of devices prepared with these dispersions appeared to be a result of the high volume fraction of highly crystalline SWCNTs.

Furthermore, the field emission cathode is expected to be able to display long emission lifetimes due to the improvement of the dispersion concentration maintaining the crystallinity of HC-SWCNTs. Future studies will focus on the hypothesis that the initial emission stability increases with a higher volume fraction of highly crystalline SWCNTs in the emitter. The planar field-emission cathode presented here has the potential to provide a new approach to energy-saving lighting in everyday life through its low power consumption.

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