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# A stand-alone flat-plane lighting device in a diode structure employing highly crystalline SWCNTs as field emitters

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We have developed and fabricated a visible-light flat plane-emission device in a simple diode structure composed of a cathode containing high crystallized single-walled carbon nanotubes (SWCNTs) dispersed in an organic $In_2O_3$–$SnO_2$ precursor solution and a non-ionic surfactant. The SWCNTs were annealed at a high temperature of 1300 K in a low-vacuum atmosphere of $10^{-1}$ Pa to obtain highly crystalline SWCNTs as field emitters. The anode, on the other hand, was fabricated with phosphors coated by ITO film and assembled with the cathode in a cavity separated by glass plates by a stable assembling process to produce a stand-alone flat plane-emission panel, with a stable and high vacuum of under $10^{-4}$ Pa. This device with its diode structure has a low driving voltage, stable current fluctuation, and low energy loss with electron emission in the cathode electrode. Furthermore, the brightness for power consumption, which is an important factor when comparing luminescent devices, was over 10,000 cd/m$^2$ with low power consumption of under 1.0 W when using a white phosphor in the simple diode panel. This cathode device in a flat plane-emission panel has the potential to provide a new means of everyday lighting in daily life.



## 1. Introduction

Extensive studies in alternative technologies and approaches for energy saving through low power consumption in daily human activities have significantly contributed to achieving improvements in energy efficiency and sustainable energy. For example, solid-state lighting devices such as light-emitting diodes (LEDs) are now widely used as luminescent systems in living and working habitats [1–4]. Many luminescent devices emitting visible light from focused positional or linear light sources produce shadows in a room. Thus, we have seen the recent development of flat-plane lighting devices–such as organic light emitting diodes (OLEDs)–for illuminating a room homogeneously [5]. Besides LEDs, attention has focused on a cathode luminescence system in the form of a cathode ray tube with attempts to use carbon nanotubes (CNTs) as a field emitter having a nanoscale needle shape with chemical stability, thermal conductivity, and mechanical strength [6]. Many studies have explored the possibility of employing CNTs as field emitters to obtain a low-power driving voltage and stable electron emission [7–9]. As an example, fabrication methods for electron emission cathodes using vertically aligned CNTs synthesized by chemical vapor deposition (CVD) or laser abrasion fabrication have been proposed [10–12], and screen printing with high viscosity submicron scale metal-particle paste has been employed to fabricate patterned field emitters [13–15]. However, these approaches only served to average out the large field-emission fluctuations of the nonhomogeneous electron emitter plane as they failed to form a uniform thin film with a homogeneous dispersion and a uniform vertical alignment for the activation of field emission using CNTs.

To obtain a homogeneous lighting plane with stable field emission in a large flat-plane device, it is important to emit electrons for field emission in a stable vacuum of $10^{-3}$ Pa using highly crystalline CNTs. In previous studies, most of the CNTs assembled in devices had crystal defects in the carbon network, rendering it difficult to obtain high electrical and physical performances with high stability in devices employing CNTs. This is thought to be due to the fact that highly crystalline CNTs–whose crystallization is difficult to control–were not used in the devices. Tohji et al. reported a method of optimizing the purification and crystallization of single-walled carbon nanotubes (SWCNTs) [16], and Iwata et al. verified the formation of highly crystalline SWCNTs by performing observations with high resolution [17].

Shimoi et al. realized an effective cathode using CNTs. This cathode had stable field emission and low field emission (FE) current fluctuation owing to the ability of CNTs to disperse uniformly in liquid media [18]. In particular, highly crystalline SWCNTs synthesized by arcing are believed to emit electrons stably at low turn-on and driving voltages in a vacuum chamber, even though their homogeneous dispersion has only recently been confirmed [19]. Furthermore, a low-viscosity solvent containing highly crystalline SWCNTs dispersed in an $In_2O_3$–$SnO_2$ (tin-doped indium oxide; ITO) precursor solution was used as the conductive matrix

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material in Ref. [19]. A non-ionic dispersant was added to facilitate the dispersion of the highly crystalline SWCNTs, and the mixture of the ITO solution, the SWCNTs, and the dispersant was agitated using ceramic beads as the milling medium.

In this paper, we report on a novel approach for achieving high power efficiency and energy efficiency using a diode structure employing highly crystalline SWCNTs that were annealed at 1300 K in a low-vacuum atmosphere of $10^{-1}$ Pa in the cathode and a phosphor covered with ITO particles in the anode. The temperature to improve the crystallinity of SWCNTs at 1300 K is referred to in the index [17]. The TEM image of improved SWCNTs and unannealed SWCNTs are shown in Fig. 1, and they are described as the deference of the lattice image. The cathode and the anode were assembled as a stand-alone flat plane-emission device in a cavity with glass panels. The fabrication and optimization of the cathode and the anode as well as the panel assembly process and the properties of the device are also discussed. This device with a diode structure has a low driving voltage, high brightness homogeneity in the plane, and a low current fluctuation under a DC voltage. Furthermore, the brightness has a high value of over 10,000 cd/$m^2$ when employing a white phosphor film with a simple diode structure in the planar panel. This flat plane-emission device has the potential to provide a new means of everyday lighting.

## 2. Experimental

### 2.1. Cathode fabrication employing highly crystalline SWCNTs

It has previously been reported that SWCNTs synthesized by arcing can be used as the source material for field emitters [20–23]. However, they could not achieve the high reliability and stability required for field-emission devices because of their low crystallinity. In response to this, Shimoi et al. attempted to employ high-purity high-crystallity SWCNTs that were dispersed by adding a low-viscosity ITO precursor solvent and a non-ionic dispersant, which was followed by shaking. The purified and high crystallized SWCNTs were expected to provide high electrical performance and serve as a source material for a field emitter owing to their homogeneous dispersion [6]. This is because highly crystalline SWCNTs have almost no surface defects in their carbon network, nor can they combine with other functional groups in the dispersant. However, some SWCNTs twisted to form bundles that were difficult to separate into single nanotubes. It was also difficult to separate SWCNTs aggregating into secondary particles into uniform single nanotubes. Furthermore, although a thin film with homogeneously dispersed highly crystalline SWCNTs is necessary for a field emission cathode plate, no method has been found for synthesizing a thin film containing SWCNTs in a vacuum chamber that exhibits homogeneous planar light emission.

Cathode fabrication employing highly crystalline SWCNTs has been described in detail, utilizing the above method with slight modifications [18]. Before fabricating the cathode, SWCNTs were annealed at a high temperature of approximately 1300 K in a low-vacuum atmosphere of $10^{-1}$ Pa to obtain highly crystalline SWCNTs. For reference, the annealed SWCNTs and SWCNTs before annealing treatment are shown in the transmission electron microscopy (TEM) image in Fig. 1, which shows highly crystalline SWCNTs in the mixture dispersed homogeneously as thin bundles comprising a few nanotubes in Fig. 1(a) and (b). As displayed in the TEM images of unannealed SWCNTs in Fig. 2(b), the well-ordered nanotube structure within the bundle disappears and the tube wall appears wavy with its carbon network distorted as a result of unannealing. This indicates that defects are partially produced at the sidewall and interstitial sidewall of the bundle.

The initial mixture was prepared by mixing the SWCNT powder with the ITO precursor (Kojundo-Kagaku Co. Ltd. Japan) and sodium *linear*-alkyl-benzenesulfonate (95%; DBS) along with ethyl cellulose (EC) (~49% ethoxy, 100 cP) in a weight ratio of about 1:600–700:1:4. Different amounts of the last component, EC, were also added. The resulting solvent mixture including SWCNTs was shaken by ultrasonication to disperse the aggregates. We succeeded in obtaining a mixture of SWCNTs dispersed as thin bundles comprising a few nanotubes. This mixture was sprayed onto a silicon wafer substrate and sintered at approximately 900 K in a vacuum to remove organic components and form bridges to produce a conductive ITO film.

The mass of the SWCNTs coating per unit area was further controlled via the number of spraying cycles to investigate both the field-emission property and the brightness efficiency of a flat-plane light emission panel. The ITO film within SWCNTs was fabricated by an activation process involving manual scratching with a milling machine employing a needle without any standing treatment of the CNTs shown in Fig. 2 so that electrons would be readily omitted at low voltages. Fig. 2(a) shows an ITO surface scratched by the needle. The darker lines indicate nicks scratched by the needle, and the SWCNTs protrude from the wall of the nick in Fig. 2(c). After the coated substrate with the SWCNTs used as a cathode plate was sintered, the cathode was ready to be analyzed after an activation process. The analyses included the determination of the electron field-emission efficiency and brightness at a low voltage.

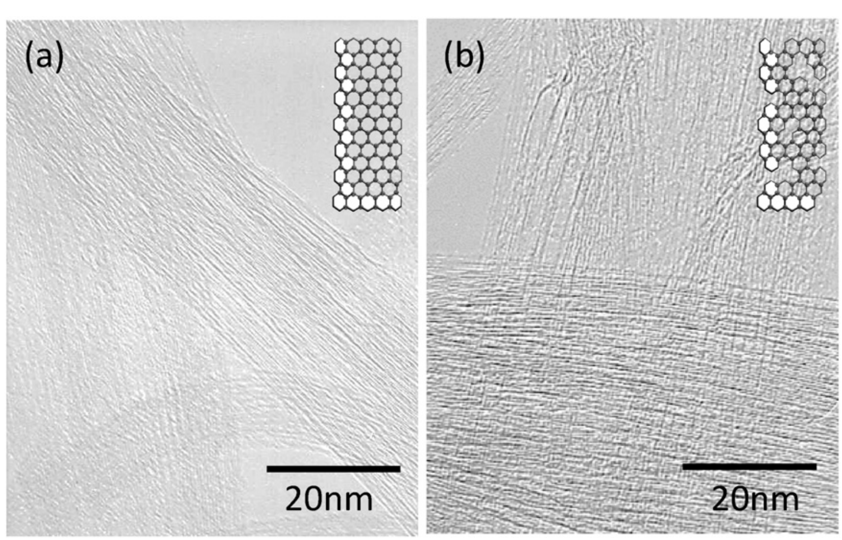


**Fig. 1.** TEM and crystal images of SWCNTs with high crystallinity after annealing (a) and before annealing (b), respectively.