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三极场发射显示器中二次印刷型碳纳米管阴极的制备及特性

李玉魁[1],王凤歌[1],曾凡光[2],卢文科[3]

(1 中原工学院 电子信息学院,郑州 450007)

(2 郑州航空工业管理学院 数理系,郑州 450015)

(3 东华大学 信息科学与技术学院,上海 201620)

摘 要:结合丝网印刷技术,研发了一种碳纳米管阴极制备法.利用双壁纳米管作为原材料,并加入细小银颗粒,制作了混合纳米管浆料.将混合纳米管浆料制作在传导电极表面,再将普通纳米管浆料印刷在混合纳米管浆料的上面.在链式烧结炉中对烘烤后的纳米管浆料同时进行烧结以除掉有机溶剂.在进行适当的后处理工艺之后,就形成了二次印刷型纳米管阴极,它能显著改善阴极的场致发射特性.制作了二次印刷型纳米管阴极的三极结构场致发射显示器.该显示器具有更高的发光亮度以及更好的发光图像亮度均匀性.与普通纳米管阴极场致发射显示器相比较,它能够将开启电场从 2.15 V/μm 降低到 1.75 V/μm,并能够将最大场发射电流从 735.8 μA 提高到1 588.5 μA.所研发的纳米管阴极制备方法具有很强的实际应用性,且制作成本低廉.

关键词:阴极;二次印刷;场发射;制备;烧结

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Preparation and Characteristic of Second-printing Type Carbon Nanotube Cathode for Triode Field Emission Display

LI Yu-kui[1], WANG Feng-ge[1], ZENG Fan-guang[2], LU Wen-ke[3]

(1 *School of Electronic Information, Zhongyuan Institute of Technology, Zhengzhou* 450007, *China*)

(2 *Department of Mathematics and Physics, Zhengzhou Institute of Aeronautical Industry Management, Zhengzhou* 450015, *China*)

(3 *School of Information Science and Technology, Donghua University, Shanghai* 201620, *China*)

Abstract: With screen-printing technique, a novel carbon nanotube (CNT) cathode preparation method was developed. Using double-walled CNT as primary material, the mixing CNT paste was fabricated, in which the minute Ag particles were included. On the mixing CNT paste printed on the conducting electrode surface, the common CNT paste was prepared. The baked CNT pastes were sintered simultaneously in the chain sintering furnace to remove the organic solvent, and the second-printing type CNT cathode was formed after the proper overvoltage post-treatment process was conducted. With the fabricated second-printing type CNT cathode, the field emission characteristics could be improved significantly. The triode second-printing CNT cathode field emission display was fabricated, which exhibited higher luminous brightness and better luminescence image brightness uniformity. Comparing with the common CNT cathode field emission display, the turn-on electric field could be reduced from 2.15 V/μm to 1.75 V/μm and

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First author: LI Yu-kui (1973—), male, associate professor, Ph. D. degree, mainly focuses on display technology, electron device fabrication, vacuum technique, nano-materials preparation and applications. Email: lyksound@sina.com

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the maximum field emission current would be enhanced from 735.8 μA to 1 588.5 μA. The developed preparation method of CNT cathode possessed considerable potential for practical applications and the fabrication cost was low.

Key words: Cathode; Second-printing; Field emission; Preparation; Sintering

0 Introduction

Carbon nanotube (CNT) was one kind of good electron emission source material owing to its special geometric shape and unique physical properties[1-3]. One of the typical applications was that the CNT had been used as cold cathode in triode field emission display (FED). With the widely adopting of screen printing technique, the fabrication of large-area and low-cost cold cathode had become easy[4-6]. However, the CNT cathode prepared by screen printing process exhibited many drawbacks, such as poor field emission performance, non-uniform electron emission capability and small emission current, etc. These problems would obstruct seriously the research development progress of FED[7-10]. For solving these technical subjects, many effective treatment methods had been reported. The mechanical rubbing method could improve the emission uniformity of CNT emitter, but the CNT layer usually was damaged easily in the treatment course. Although the plasma treatment method would enhance the electron emission ability of CNT emitter to form a large emission current, the treatment cost was usually too expensive. For improving the field emission performance, the adhesive taping method was an effective technology, however, the electron-emission uniformity and stability of CNT emitter was not satisfactory, and the fabrication process was complex. Furthermore, all these above-mentioned methods were not suitable for the preparation on large-area CNT cathode[11-16]. In this paper, a new CNT cathode preparation method was proposed basing on the effective screen printing technique, and the detailed fabrication process was also presented. The mixing CNT paste and the common CNT paste were fabricated in sequence on the conducting electrode to form the second-printing type CNT cathode, and the field emission characteristics could be improved significantly.

1 Experimental

1.1 Preparing of CNT pastes

Two kinds of CNT pastes were formed, which were the mixing CNT paste and the common CNT paste, respectively. The purified double-walled CNT was adopted, which the length was about 10～25 μm and the diameter of single CNT was greater than 15 nm. For the mixing CNT paste, the CNT powder, the minute Ag particle and the terpineol were first mixed to form the mixture slurry, in which the CNT content was approximate 5% (in weight). The mixture slurry was heated to 75℃, and the ethyl cellulose was added. After sufficient stirring process the mixing CNT paste was obtained. For the common CNT paste, the CNT powder, the terpineol and the ethyl cellulose were blended firstly, and the formed slurry was adequate stirred at room temperature in the magnetic stirrer. So the common CNT paste was also prepared.

1.2 Fabrication of second-printing type CNT cathode

Fig. 1 showed the structure schematic diagram of second-printing type CNT cathode.

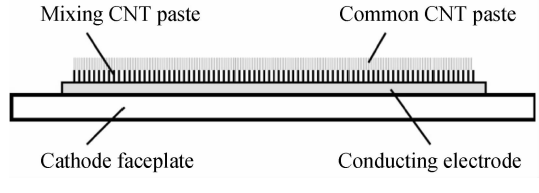


Fig. 1 The structure schematic diagram of second-printing type CNT cathode

1) The indium tin oxide (ITO) film covered on the cathode faceplate surface was etched to form the bar conducting electrode. The used etching solution was: HCl (36.5%) + HNO_3 (67.5%), and the etching temperature was maintained at 55℃.

2) The mixing CNT paste was screen-printed on the conducting electrode surface, and then was baked in the special CNT automatic electric oven. The baking time was about 35 minutes and the constant baking temperature was 230℃.

3) On the baked mixing CNT paste surface, the common CNT paste was fabricated with effective screen printing technique. The similar baking process was also carried out in the special CNT automatic electric oven, in which the only difference was that the baking temperature was changed to 255℃.

4) The sintering process was conducted for the printed CNT paste simultaneously in the chain sintering furnace. The maximum sintering

temperature was 525℃ and the total sintering time was about 75 minutes. In the sintering course, the high purity argon gas was always used as protective gas for avoiding that the CNT was oxidized.

5) For the sintered CNT cathode, the overvoltage post-treatment process was performed in the field emission test system, in which the system vacuum level was 1.5×10^{-3} Pa. The forward voltage was applied between the anode electrode fabricated on the anode glass and the conducting electrode on the cathode faceplate. The formed electric field intensity was about 3.0 V/μm and the maintaining time was 3 minutes.

1.3 Full-sealing of triode FED

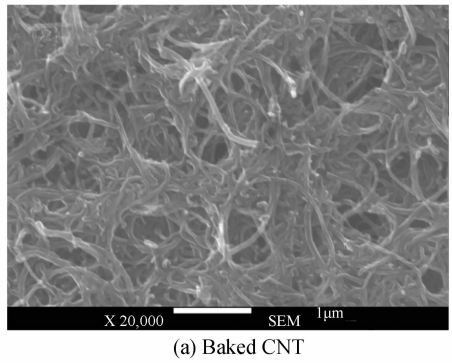
The phosphor was printed on the patterned ITO electrode of anode faceplate to form the luminous layer. The grid fabricated on cathode faceplate was used to control the electron emission of second-printing type CNT cathode, and the glass frame was employed to separate the anode and cathode faceplate. The glass frit was sintered to seal the vacuum chamber of triode FED. So the second-printing CNT cathode FED prototype was developed. For comparing, the common CNT paste was screen-printed directly on the bar ITO electrode to form the cold cathode, and the common CNT cathode FED prototype was also fabricated with the similar manufacture process.

2 Results and discussion

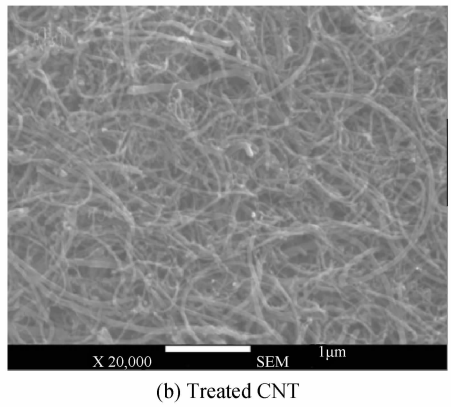
2.1 SEM photo of CNT surface morphology

The SEM photos of surface morphology for second-printing type CNT cathode sample were presented in Fig. 2.

Thereinto, Fig. 2(a) showed the SEM photo of baked CNT. Seen from the photo, Many CNTs were adhered each other. On the one hand, due to the adhesion action of organic slurry, the adhered CNTs could cover the conducting electrode surface. On the other hand, a large amount of organic slurry existed on the CNT surface, which directly led to the appearing of CNT blocks agglomerating phenomenon. Many large holes had been detected among the adjacent CNT blocks and much CNT ends were also buried in the CNT blocks. The SEM photo of treated CNT was illustrated in Fig. 2(b). Seen from the Fig. 2(b), several results could be obtained.



(a) Baked CNT



(b) Treated CNT

Fig. 2 SEM photos of surface morphology for second-printing CNT cathode

1) The good distributing uniformity for the CNTs layer had been confirmed. Just because the proper high temperature sintering process was conducted in the CNT cathode preparation course, the organic slurry on CNT layer surface had been removed completely, and the obvious CNT agglomerating blocks had also become invisible.

2) The CNTs were attached tightly to the conducting electrode, in which a part of CNTs were derived from the mixing CNT paste, and the rest of CNTs would come from the common CNT paste. For the second-printing type CNT cathode, the common CNT paste was fabricated on the mixing CNT paste. It would mean that the number of CNT had been increased in CNT layer. Although the different CNTs already could not be distinguished, it was undoubted that the field emission current would be enhanced due to the increasing CNT emitter.

3) Much CNTs ends had been exposed, which indicated that more electrons would be emitted from the CNT layer. The overvoltage post treatment process was employed in the cathode preparation course, not only the loose CNTs would be eliminated, but also the remained organic slurry adhered to the CNT surface would be evaporated

owing to the generated excess current. Of course, it was beneficial for improving the electron-emitting ability of CNT cathode.

2.2 Field emission characteristic

The measured field emission curves of two kinds of triode FED prototype were illustrated in Fig. 3.

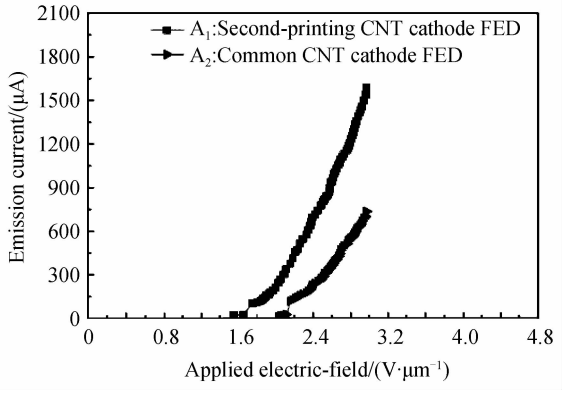


Fig. 3 The measured field emission curve of (A_1) second-printing CNT cathode FED and (A_2) common CNT cathode FED

Thereinto, the curve (A_1) showed the field emission characteristic of second-printing CNT cathode FED, while the curve (A_2) demonstrated the functional relationship for common CNT cathode FED. The anode voltage was fixed with 1.65 kV in the measuring course. Seen from the presented curves, some results could be achieved.

1) The second-printing CNT cathode FED possessed lower turn-on electric field. With the same measuring condition, the turn-on electric field for second-printing CNT cathode FED was 1.75 V/μm, while the one for common CNT cathode FED was 2.15 V/μm.

2) Under the same electric field (was 2.39 V/μm), the field emission current of second-printing CNT cathode FED was 692.6 μA, while that of common CNT cathode FED was 228.3 μA. The maximum field emission current for second-printing CNT cathode FED had reached 1588.5 μA, but that for common CNT cathode FED only was 735.8 μA. It would mean that the second-printing CNT cathode FED possessed larger field emission current.

3) For second-printing CNT cathode FED, the increment of field emission current was approximate 663 μA when the electric field was enhanced from 2.29 V/μm to 2.77 V/μm. But for the common CNT cathode FED, the field emission current was increased only with 410 μA when the electric field was changed from 2.42 V/μm to 2.91 V/μm. Meanwhile, the field emission current had been close to the value of maximum field emission current, which would indicate that the further increasing of field emission current had become impossible. If the external operation voltage continued to raise, the field emission instability phenomenon would occur. The field emission curve could become much steep, which would imply that the second-printing CNT cathode FED possessed better field emission characteristic. We think that the second-printing CNT cathode would play a key role for improving the field emission performance of triode FED prototype.

In the CNT cathode preparation course, the high temperature sintering process was conducted, which the main function was to remove the organic solvent on CNT layer surface. However, the organic solvent residing on the interface between the conducting electrode and the CNT in the CNT layer inner could not be disposed entirely. Otherwise, all the CNT would fall off from the conducting electrode surface. Although the conducting electrode and the CNT all owned good conducting performance, the question was that the poor electrical contact existed in the interface due to the residual organic solvent, which would effect directly the field emission property of triode FED. For the second-printing type CNT cathode, the minute Ag particles were added in the mixing CNT paste, which was fabricated on the conducting electrode surface. In the sintering course, the Ag particle would be melted because of the high sintering temperature. On the one hand, the solidified Ag particle could be attached solidly to the conducting electrode surface; on the other hand, some CNTs were also embedded in the solidified Ag particle. Depending on the Ag particle, the cathode potential could be conducted smoothly from the conducting electrode to the CNT. So the better electrical contact could be confirmed in the second-printing type CNT cathode. Of course, it was helpful to improve the field emission characteristic of triode FED prototype. Moreover, the common CNT paste was covered on the mixing CNT paste, which the phenomenon of electron-emitting from the Ag particle would be avoided.

2.3 Luminescence image

The typical luminescence images of triode FED prototype were illustrated in Fig. 4.

Thereinto, Fig. 4(a) showed the luminescence image for the common CNT cathode FED, while that for the second-printing CNT cathode FED was

presented in Fig. 4(b). Seen from the images, several obvious results would be gained.

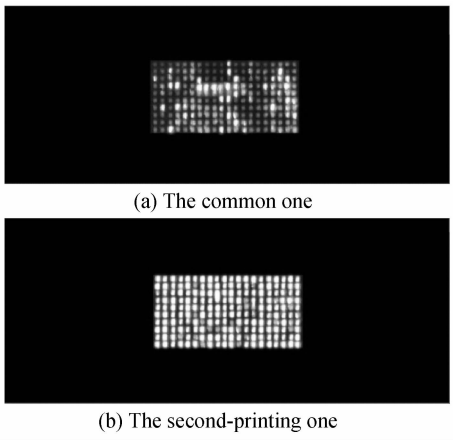


Fig. 4 The typical luminescence images for the common CNT cathode FED and for the second-printing CNT cathode FED

1) The anode pixels on anode faceplate could be normal lightened for both the second-printing CNT cathode FED and the common CNT cathode FED. As we know, without the high speed electrons emitted from CNT cathode, the visible light of triode FED would not be generated. So it would indicate that either the second-printing type CNT cathode or the common CNT cathode could supply lots of electrons in the vacuum environment. Meanwhile, it was also shown that the fabrication of second-printing type CNT cathode was feasible.

2) Comparing with the two given images, the significant difference had been confirmed. Seen from the image brightness, the luminous brightness of common CNT cathode FED was low, while the one of second-printing CNT cathode FED was high. Seen from the luminescence image brightness uniformity, the common CNT cathode FED had poor brightness uniformity. Only part of anode pixels could give out light, while another part of anode pixel was not lighted at all. And for the lightened anode pixels, the luminous brightness of some anode pixels was higher obviously than that of other anode pixels. However, the second-printing CNT cathode FED exhibited better image brightness uniformity. All the anode pixels could be lighted, and the luminous brightness difference of different anode pixels also was not significant. These above-mentioned results showed that the second-printing type CNT cathode could supply larger field emission current. Due to the overvoltage post treatment in the second-printing type CNT cathode preparation course, much CNT ends could protend to the CNT layer surface, which would carry out the proper electron emission. Of course, it was natural that the second-printing CNT cathode FED could keep larger emission current. Furthermore, the electron-emitting ability of different CNTs in the second-printing CNT cathode tended to become same on the whole because the CNT was evenly distributed on the conducting electrode surface. It was also advantageous to improve the luminescence image brightness uniformity of the second-printing CNT cathode FED.

Fig. 5 showed the luminous brightness curves of triode FED, in which the brightness curve of the second-printing CNT cathode FED was illustrated in Fig. 5(B_1) and the one of the common CNT cathode FED was given in Fig. 5(B_2). The maximum luminous brightness for the second-printing CNT cathode FED was about 1 576 cd/m^2, but that for the common CNT cathode FED was approximate 793 cd/m^2. Under the same electric field of 2.61 V/μm, the measured luminous brightness of the second-printing CNT cathode FED was 872.3 cd/m^2, which was higher than the one of the common CNT cathode FED (was 316.5 cd/m^2). So it was confirmed that the fabricated second-printing type CNT cathode could remarkably enhance the image performance of triode FED.

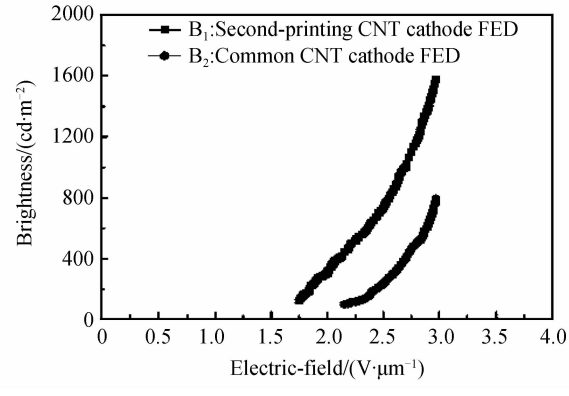


Fig. 5 The luminous brightness curves of (B_1) the second-printing CNT cathode FED; (B_2) the common CNT cathode FED

2.4 Real photo of the second-printing CNT cathode FED

The real photo of the second-printing CNT cathode FED prototype was presented in Fig. 6. Some typical specifications of the triode FED prototype were as follows. The outer dimension was 160 mm (length)×50 mm (width). On anode faceplate the anode pixels were arranged in the form of a 10 (row)×20 (column) matrix. And the area of one anode pixel was 600 μm×600 μm.

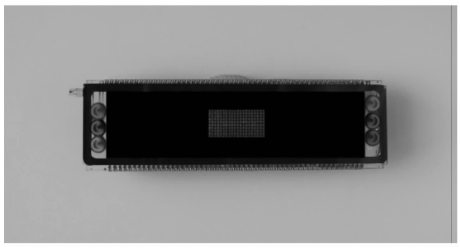


Fig. 6 The real photo of the second-printing CNT cathode FED prototype

The fabricated second-printing type CNT cathode on cathode faceplate was packaged in the vacuum chamber of triode FED. In the cathode preparation course, there was no any physical contact with the CNT cathode, which the damage for CNT layer would be avoided. Moreover, for the developed preparation process there was no any restriction for the cathode area, which seemed to imply that the method was very suitable for the fabrication of large-area CNT cathode.

3 Conclusions

1) A novel CNT cathode preparation method was proposed with effective screen-printing technique. The mixing CNT paste and the common paste were screen-printed in proper sequence on the conducting electrode surface of cathode faceplate. After the sintering process for the fabricated CNT layer, the overvoltage post-treatment process was conducted. So the second-printing type CNT cathode was formed, which could improve remarkably the field emission characteristics. The presented cathode preparation method had the merits of simple operation, low cost and the large-area production feasibility.

2) An addressable second-printing CNT cathode FED prototype was full-sealed firstly, which possessed large field emission current, higher luminous brightness and better image brightness uniformity. Comparing to the common CNT cathode FED, the turn-on electric field could be reduced from 2.15 V/μm to 1.75 V/μm, the maximum field emission current would be enhanced from 735.8 μA to 1 588.5 μA, and the maximum luminous brightness could be increased from 793 cd/m^2 to 1 576 cd/m^2.

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