# Application of ZnO nanopillars and nanoflowers to field-emission luminescent tubes*

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**Abstract:** Zinc oxide (ZnO) nanopillars on a ZnO seed layer and ZnO nanoflowers were synthesized by electrochemical deposition on linear wires. The morphologies and crystal orientation of the ZnO nanostructures were investigated by a scanning electron microscopy and an X-ray diffraction pattern, respectively. Detailed study on the field-emission properties of ZnO nanostructures indicates that nanopillars with a high aspect ratio show good performance with a low turn-on field of 0.16 V/$\mu$m and a high field enhancement factor of $2.86 \times 10^4$. A luminescent tube with ZnO nanopillars on a linear wire cathode and a transparent anode could reach a luminance of about $1.5 \times 10^4$ cd/m$^2$ under an applied voltage of 4 kV.

**Key words:** ZnO nanopillars; electrochemical deposition; field emission; luminescent tube
**DOI:** 10.1088/1674-4926/33/4/043003 **EEACC:** 2520

## 1. Introduction

Developed over two decades ago, cold electron sources based on field emission have such advantages over thermoelectronic emission or semiconductor diodes as high brightness, a larger color gamut, a long lifetime and are free of hazardous substances[1−4]. A comprehensive overview of the various applications in field-emission displays, lighting elements, electron microcolumns in lithography, mass spectrometry for space exploration and radio frequency devices etc, is presented by Xu and Huq[5]. So far, carbon nanotubes (CNTs) are promising cold field-emitter candidates. Recently, a CNT-based lighting source was successfully developed. The application of CNTs to electron sources for lighting element tubes is reported by Saito *et al.*[6]. Also, Bonard *et al.*[7] reported the application of CNTs grown on metallic wire in luminescent tubes, and more recently the lighting elements of the four primary colours were produced and a brightness >10 000 cd/m$^2$ was demonstrated[8].

Meanwhile, one-dimensional nanoscale materials have also appeared to be quite competitive. Zinc oxide (ZnO) is a transparent semiconductor with a wide band gap of 3.37 eV and a large excited binding energy of 60 meV at room temperature[9−12]. Its band bending, which usually favors field emission by lowering the surface barrier and bringing more electrons to the bottom of conduction band, can be quite dramatic under high field. A striking advantage of ZnO lies in its high field-emission stability, in comparison to the well-studied CNTs, particularly in poor vacuum and low air pressure operating conditions[13]. Recently, it has been found that the synthesis methods and field-emission performances of ZnO nanostructures have been reported[14−18].

In the present work, we synthesize two different types of ZnO nanostructures on a linear metallic wire, including nanopillars and nanoflowers, using electrochemical deposition, and the field-emission properties of ZnO nanostructures are studied. In particular, for future practical applications, we try to assemble a field-emission luminescent lighting tube with a linear cathode and a cylindrical anode, and the results are quite encouraging.

## 2. Experimental methods

All the chemicals (Shanghai Chemicals Co. Ltd.) were of analytical grade and used as received. Prior to the electrochemical deposition, the nickel wires were ultrasonically washed for 10 min in an acetone, absolute ethylalcohol, and deionized water, respectively. After that, the ZnO seed-layer films were deposited on nickel wires using the sol–gel method. Zinc acetate dihydrate ($Zn(CH_3COO)_2{\cdot}2H_2O$) was briefly dissolved in a mixed solution of ethanolamine ($NH_2CH_2CH_2OH$) and 2-methoxyethanol ($(CH_3)_2CHOH$) at a concentration of 0.75 mol/L. Then the resultant solution was stirred at 60 ℃ for 30 min to yield a homogeneous and clear colloid solution. The clean nickel wires were dipped into the colloid solution for 5 min, and subsequently dried in a furnace at 350 ℃ for 30 min. Details of the electrochemical deposition have been given elsewhere[19]. As shown in Fig. 1, the ZnO nanostructures were grown by amperometry potentiostatically at −1.20 V (with respect to an Ag/AgCl reference electrode) for 4 h on linear substrates in a three-electrode cell immersed in a water bath held at 70 ℃. A nickel wire and a stainless steel circular cylinder served as the working electrode and counter electrode, respectively. The electrolyte consisted of a zinc nitrate

* Project supported by the National High Technology Research and Development Program of China (No. 2008AA03A313), the National Natural Science Foundation of China (No. 61106053), and the State Key Laboratory of Electronic Thin Films and Integrated Devices, China (No. KFJJ200916).
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Received 16 September 2011, revised manuscript received 29 November 2011 

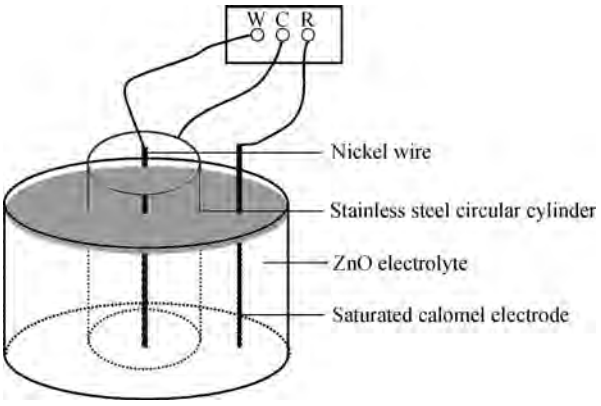


Fig. 1. Schematic of the ZnO nanostructures grown on metallic nickel wire by electrochemical deposition.

$(Zn(NO_3)_2{\cdot}6H_2O)$ solution with a concentration of 0.01 mol/L mixed with 0.02 mol/L sodium hydroxide (NaOH). Thus, the general scheme of the electrochemical deposition of ZnO from aqueous $Zn(NO_3)_2$ solution is supposed as follows:

$$Zn^{2+} + NO_3^- + 2e^- \rightarrow ZnO + NO_2^-, \quad (1)$$

$$5Zn^{2+} + NO_3^- + 2H_2O + 8e^- \rightarrow 5ZnO + NH_4^+. \quad (2)$$

The morphology of the as-grown samples was observed with scanning electron microscopes (SEM, Hitachi 3000), and the crystal structure of the products was characterized by X-ray diffraction (XRD, Philips X'Pert, CuK$\alpha$ line: 0.15419 nm). The field-emission measurements were carried out in a vacuum system with a base pressure of $10^{-5}$ Pa. A cylinder-shaped quartz glass tube with ITO and phosphor film was used as the anode. Two kinds of cathodes were used in the measurement. One was a nickel wire coated with a ZnO seed layer and nanostructure, and the other was a ZnO nanostructure on a nickel wire. The cathode was fixed in the centre of cylinder-shaped anode using two elasticity metal tongs. The spacing between the phosphor screen anode and the cathode was 10 mm. The $J$–$E$ curve and the dependence of the luminance on the applied voltage ($L$–$V$ curve) could be recorded automatically with a self-developed signal acquisition system.

## 3. Results and discussion

Figure 2 shows the SEM images of the ZnO samples by electrochemical deposition. From the inserted high-magnification SEM image (Fig. 2(a)), we can see that the obtained ZnO nanopillars are all hexagonal, straight and relatively vertical to the substrate, with average diameters of about 300 nm and lengths of about 5 $\mu$m. But the SEM image of Fig. 2(b) shows that the ZnO nanoflowers are made up of one centre about 400 nm in diameter and four leaves about 800 nm in length. From the above observations, it is clear that the morphologies of electrochemically deposited ZnO vary from nanopillars to nanoflowers because of the existence of the seed layer.

Figure 3 shows the XRD patterns of the electrochemically deposited ZnO nanopillars and nanoflowers. From these XRD data, the characteristic diffraction peaks of the hexagonal wurtzite-structured ZnO are indexed as (100), (002), (101)

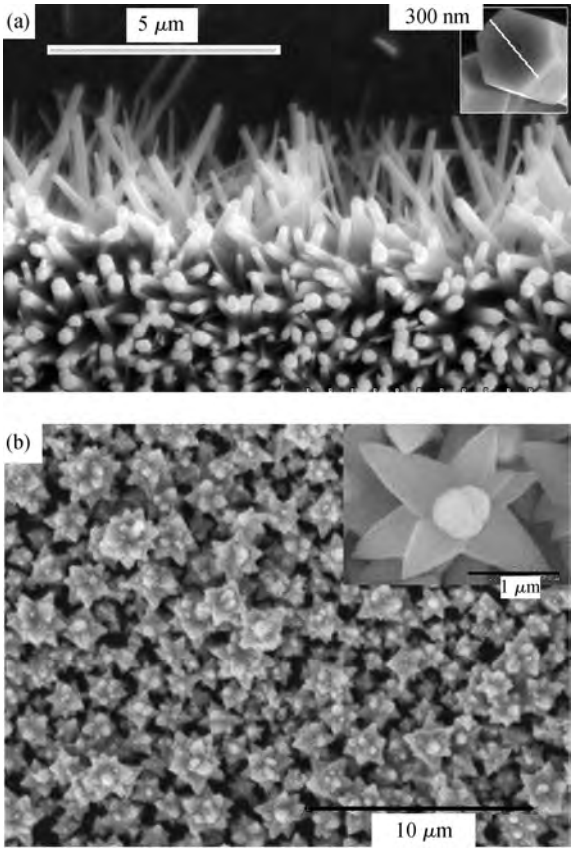


Fig. 2. SEM images of (a) ZnO nanopillars grown on a seed layer, and (b) ZnO nanoflowers grown without a seed layer.

and (102). But, for the nanopillars electrochemically deposited on a seed layer, the diffraction peak intensity ratio of (002) is stronger than that of the ZnO nanoflowers, indicating their highly $c$-axis orientation. This corresponds to the results of the SEM image.

It is known that there are many factors (such as reduction potential, substrate and capping agents) that affect the crystal characteristics of ZnO nanostructures produced by the electrochemical deposition process. The presence of a ZnO seed layer for the formation of $c$-axis oriented ZnO nanostructures has been investigated in previous studies[20–22].

Field-emission measurements are carried out using a cylinder-shaped configuration. The ZnO nanostructures on metallic nickel wires and a cylinder-shaped quartz glass tube coating with transparent ITO and phosphor films are used as the cathodes and anodes, respectively. The distance between the cylinder-shaped anode and the centric cathode wire is 10 mm. When a high voltage is applied to the anode, electrons will be emitted from the cathode wires and excite the phosphor screen.

The emission current is measured by applying a voltage, which increases from 1 to 5.5 kV. The dependencies of the field-emission current density on the applied electric field ($J$–$E$) are shown in Fig. 4. The turn-on fields (defined as the applied field to draw an emission current density of 10 $\mu$A/cm$^2$) are 0.16 V/$\mu$m for the ZnO nanopillars and 0.24 V/$\mu$m for the ZnO nanoflowers, respectively, which are lower than those of the ZnO nanostructures ($\sim$9–17 V/$\mu$m for 10 $\mu$A/cm$^2$) grown by electrochemical deposition[23]. And the threshold fields (de-

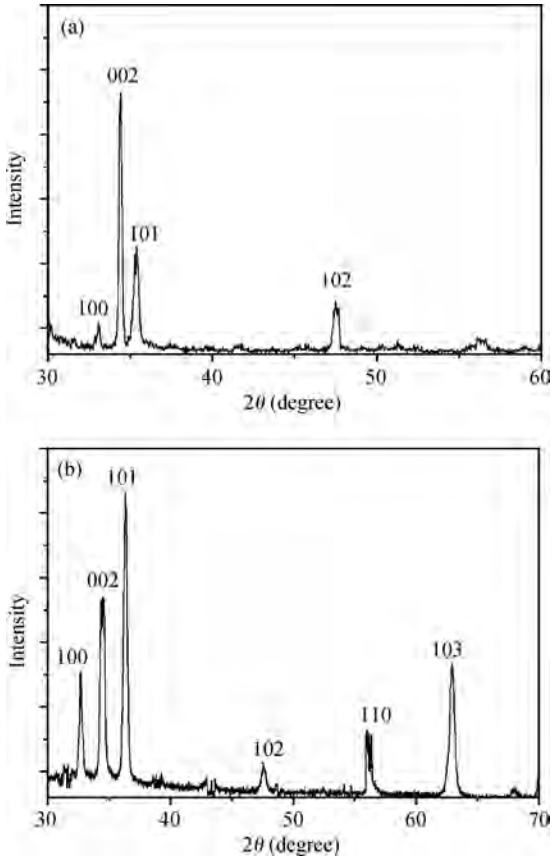


Fig. 3. XRD patterns of (a) ZnO nanopillars grown on a seed layer, and (b) ZnO nanoflowers grown without a seed layer.

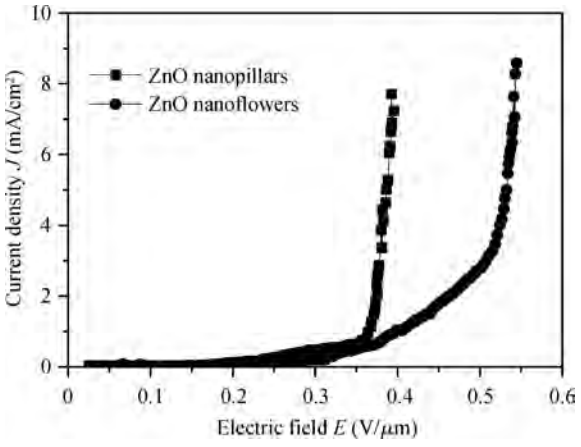


Fig. 4. Dependencies of the field-emission current density on the applied electric field ($J$–$E$) of ZnO nanopillars and nanoflowers.

fined as the applied field where an emission current density arrives at 1 mA/cm$^2$) of the ZnO nanopillars and nanoflowers are 0.36 and 0.42 V/$\mu$m, respectively. The emission current density is achieved about 8 mA/cm$^2$ at 0.4 V/$\mu$m of the ZnO nanopillars, which is lower than that of the ZnO nanoflowers at 0.54 V/$\mu$m. This means that the field-emission properties of ZnO nanopillars are better than those of ZnO nanoflowers.

Generally, it is well agreed that field emission mainly depends on the tip morphology and large aspect ratio of the nanostructures. Since the ZnO nanopillars have a much larger aspect

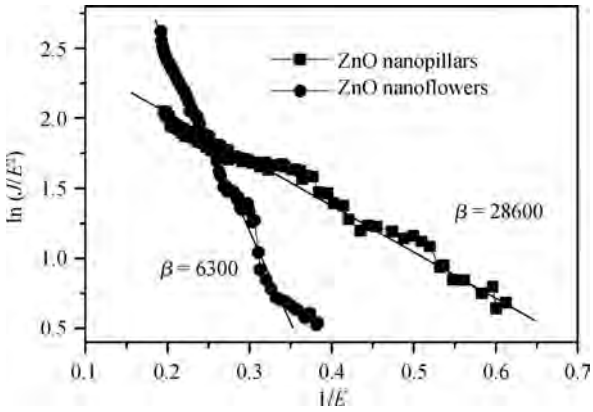


Fig. 5. Corresponding Fowler–Nordheim plots of the ZnO nanopillars and nanoflowers.

ratio compared to the ZnO nanoflowers, it is reasonable that the electrons can be more easily emitted from the nanopillars based on the seed layer in our case.

According to the Flower–Nordheim (F–N) theory, the relationship between current density ($J$) and applied electric field ($E$) can be described as follows[24]:

$$J = A\left(\frac{\beta^2 E^2}{\phi}\right)\exp\left(-\frac{B\phi^{3/2}}{\beta E}\right), \tag{3}$$

where $A = 1.54 \times 10^{-10}$ (A·eV/(V$^2$·$\mu$m)), $B = 6.83 \times 10^3$ (V/(eV$^{3/2}$·$\mu$m)), and $\phi$ is the work function about 5.4 eV for ZnO[25]. $\beta$ is the field-enhancement factor, which is associated with the magnitude of the electric field at the emitting surface by the relation $E_{(\mathrm{local})} = \beta E$, where $E_{(\mathrm{local})}$ is the local electric field at the emitting top surface. The F–N plots for the samples are shown in Fig. 5. These approximate straight lines indicate that the emitting electrons mainly result from field emission. From the averaged slope of the $\ln(J/E^2)$ versus $1/E$ plots, the $\beta$ values can be estimated, and are shown in Fig. 5. It is interesting in our case that there is such a large $\beta$ value of the ZnO nanostructures, which is caused by the cylindrical geometry. The total $\beta$ value can be expressed as

$$\beta = \beta_{\mathrm{ZnO}}\beta_{\mathrm{cylinder}} = \beta_{\mathrm{ZnO}}\frac{V}{R_1 \ln\dfrac{R_2}{R_1}}, \tag{4}$$

where $R_2 = 1 \times 10^4$ $\mu$m (the distance of the anode to the cathode) and $R_1 = 150$ $\mu$m (the radius of the cathode). The $\beta_{\mathrm{ZnO}}$ values are estimated to be about 1802 for the ZnO nanopillars and about 397 for the ZnO nanoflowers, respectively. The vertical growth of the ZnO nanopillars means they have a better ability to enhance the local field at the emitting surface and reduce the turn-on electric field. The above results indicate that the cylindrical configuration produces better field emission than the parallel-plate configuration.

A luminescent tube is fabricated with a cylinder-shaped quartz glass anode and ZnO nanopillars grown on the nickel wire cathode, and the lighting photo of the sample tube is shown in Fig. 6. The luminance of the tube achieves about 15000 cd/m$^2$, measured by a photometer under the conditions of a 4 kV applied voltage, and yields an emission current den-

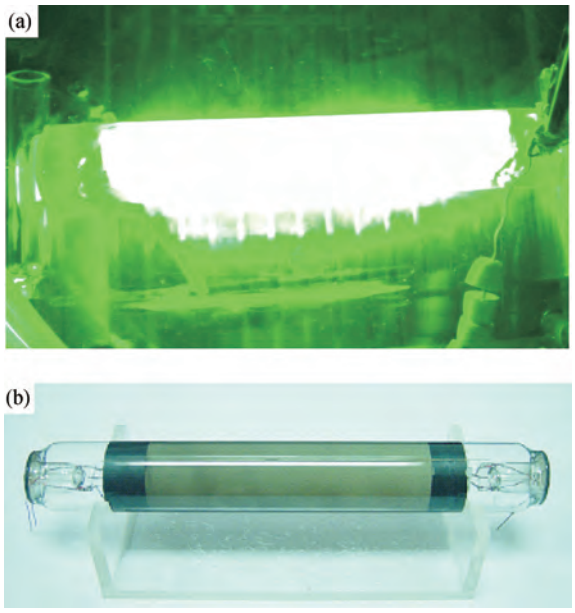


Fig. 6. (a) A luminescent tube fabricated with a metallic cathode wire of ZnO nanopillars, and (b) a cylinder-shaped anode.

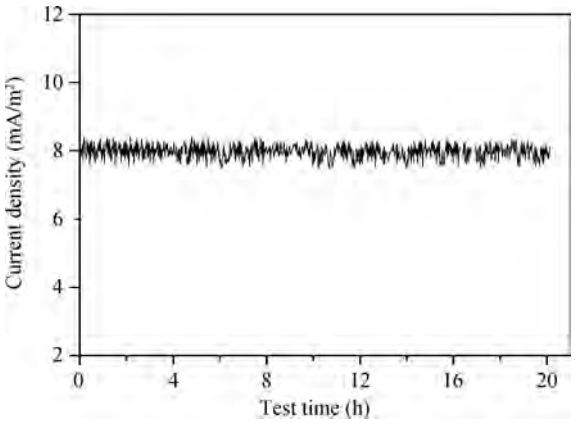


Fig. 7. Emission stability of a luminescent tube with a ZnO nanopillar cathode.

sity of 8 mA/cm$^2$. The luminance efficiency, $\eta$ (lm/W), is defined as

$$\eta = \frac{\pi A_1 L}{VI} = \frac{\pi A_1 L}{A_2 VJ}, \tag{5}$$

where $A_1$ and $A_2$ are the anode and cathode areas, i.e. the phosphor-coated and ZnO nanostructure-coated areas (m$^2$), respectively. $L$ is the measured luminance (cd/m$^2$). We estimated $\eta = 9.8$ lm/W at $V = 4$ kV, $J = 8$ mA/cm$^2$, $A_1 = 62.8$ cm$^2$, $A_2 = 0.942$ cm$^2$ and $L = 15000$ cd/m$^2$ in our device. The emission stability of a luminescent tube with a ZnO nanopillar cathode is given in Fig. 7. The stability measurement was performed for 20 h with an initial current density of about 8 mA/cm$^2$, and it was clear that no obvious decrease can be seen after 20 h. Therefore, the ZnO nanopillars grown on metallic wire should be considered as a promising candidate in future device applications such as high-brightness electron sources.

## 4. Conclusion

In conclusion, we successfully synthesized ZnO nanopillars on a seed-layer film and nanoflowers on metallic nickel wires via simple electrochemical deposition. The seed layer induces the highly $c$-axis orientation of the ZnO nanopillars, which leads to a high aspect ratio. Efficient field emission indicates that the cathode wires of the ZnO nanopillars and nanoflowers possessed good performance with low turn-on and threshold fields. The experimental results demonstrate that ZnO nanopillars grown on metallic wires by electrochemical deposition could be a significantly promising method for making field-emission electroluminescent light sources.

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