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Low-field electron emission from pinaster-like MoO_2 nanoarrays as two-stage emitters*

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Low-field electron emission is obtained from the pinaster-like MoO_2 nanoarrays. The turn-on field of the pinaster-like MoO_2 nanoarrays is found to be as low as $2.39\,V/\mu m$ with the current density of $10\,\mu A/cm^2$. The enhancement factor is extracted to be 3590 from the Fowler–Nordheim plot. These excellent emission properties are attributed to the special structure of the pinaster-like MoO_2 nanoarrays and confirmed by the calculation in the frame of the two -stage model. Our results show that the pinaster-like MoO_2 nanoarrays are promising candidate in realizing field emission displays.

Keywords: field emission, molybdenum dioxide, enhancement factor
PACC: 7900, 8116, 2110F

Field emission is technologically important for vacuum microelectronic devices such as field emission displays, x-ray sources, microwave devices, etc.[1,2] One-dimensional nanomaterials, such as nanotubes, nanowires, nanobelts are promising materials served as the electron emission source due to the high aspect ratio of the length to the diameter. The local electrical field at the tip of the needle-shaped emitters can be enhanced significantly to the mean electrical field, which is quantified by the field enhancement factor β. In order to extract an appreciable field emission current at low applied electric field, a high enhancement factor β is desired for emitter applications. Bonard *et al*[3] have studied the field emission properties of an individual carbon nanotube and their experimental result is consistent with the Edgcombe and Valdré model. The enhancement factors of aligned or misaligned emitters are more complicated because the electric field on one emitter can be screened by the proximity of neigbouring emitters.[4−6]

One way to obtain a low turn-on field is to design a suitable structure of the emitters. Recently, a very high enhancement factor was observed from the ZnO nanowires or the nanotubes grown on the carbon cloth.[7,8] Jo *et al*[8] reported an ultrahigh enhancement factor, as high as 4.11×10^4, from ZnO nanowires-carbon cloth nanotube system. The high enhancement factors were due to the multi-stage structure of the emitter.[9] However, the carbon fibre is lying on the substrate, and nonuniformity in length suggests that the carbon cloth is not suitable for the practical field emission device.

MoO_2, a promising material for applications in catalysts, sensors, electro-chromic and recording devices,[10,11] has been investigated as a cathode emitter. In this article, a new structure of pinaster-like MoO_2 nanoarrays grown vertically to the substrate are synthesized and the field emission from the MoO_2 nanoarrays with a low turn-on field is realized. The turn-on field is as low as $2.39\,V/\mu m$ with the current density of $10\,\mu A/cm^2$.

Pinaster-like MoO_2 nanoarrays were fabricated via a simple thermal evaporation method. A silica wafer was placed above a tungsten boat loaded with Mo powder, which served as the Mo source, the distance between the Mo powder and the silica substrate being about 5 mm. And the tungsten boat was placed in a vacuum chamber with a pressure of 8×10^{-4} Pa. Then the tungsten boat was heated to 1300°C and kept for 3 h. When the boat was cooled down to room temperature, a grey layer was deposited on the surface of the silica wafer. The morphology of the prod-

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uct was examined by scanning electron microscopy (SEM). The crystal structure of the sample was characterized by x-ray diffraction (XRD) and transmission electron microscopy (TEM).

Figure 1 shows the XRD pattern of the pinaster-like MoO_2 nanoarrays. The diffraction peaks can be well indexed based on the monoclinic MoO_2 structure with the lattice constants $a = 0.5608\,\text{nm}$, $b = 0.4842\,\text{nm}$, $c = 0.5517\,\text{nm}$ and $\beta = 119.7$ (JCPDS: 330929). Figures 2(a) and 2(b) are the SEM images showing the typical feature of the pinaster-like MoO_2 nanoarrays. It can be seen that the pinaster-like MoO_2 has a trunk with a diameter of 0.8–3 μm and a length about 12μm. The diameter of the trunk gradually decreases along the length. There are a large amount of MoO_2 nanowires with 8nm in diameter protruding from the MoO_2 trunk. It should be noted that there is a relative long MoO_2 nanowire with a length of 1–2 micron at each tip of the MoO_2 trunk. These MoO_2 nanowires can be potential field emission sites. The highly magnified SEM image (Fig.2(c)) shows in detail the morphology of the pinaster-like MoO_2. The density of the pinaster-like MoO_2 can be estimated to be $1\times10^7/\text{cm}^2$. Figure 2(d) is the TEM image of the individual MoO_2 nanowires, showing that they are single crystallines grown along the direction parallel to the (110) plane.

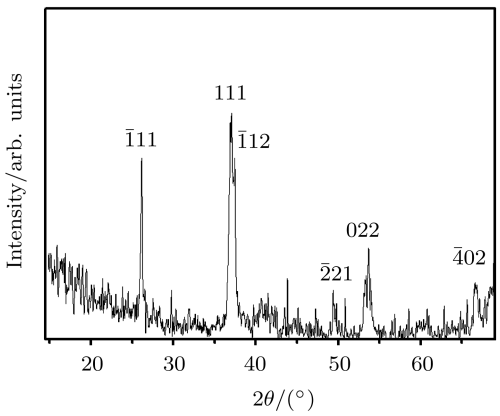


Fig.1. XRD pattern of the pinaster-like MoO_2 nanoarrays.

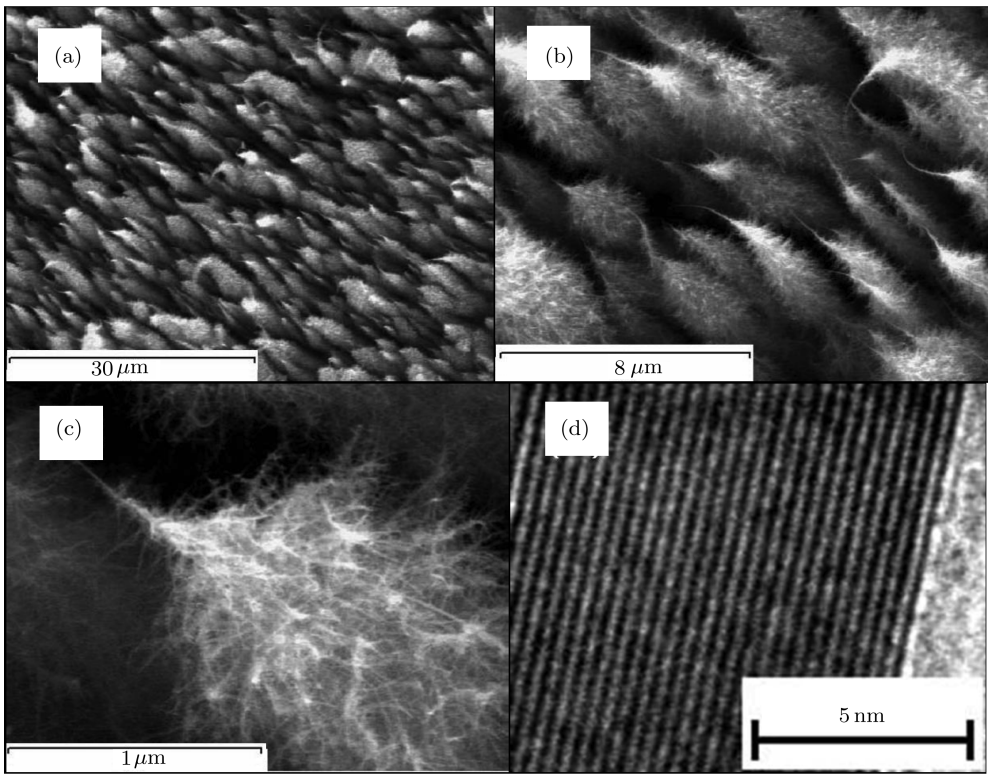


Fig.2. (a) SEM image of the pinaster-like MoO_2 nanoarrays. (b) High magnification of SEM image of the pinaster-like MoO_2 nanoarrays. (c) SEM image of the tip of the pinaster like MoO_2.(d)TEM image of the MoO_2 nanowires.

Because no metallic catalysts were used in the original growth process, the growth mechanism of the pinaster-like MoO_2 nanoarrays cannot be explained by a conventional vapour–liquid–solid model.[12] The process of pinaster-like MoO_2 nanoarrays growth may be dominated by the vapour–solid (V–S) mechanism, in which the oxide vapour directly deposits on a substrate at a lower temperature zone.[13] At the beginning, evaporation occurred at the surface of the Mo powder when the tungsten boat was heated to high temperatures. The Mo molecules reacted with the residual oxygen in the vacuum chamber, and transported to the silica substrate at low temperatures. A trunk of the MoO_2 first formed on the silica substrate, then MoO_2 nanowires with small diameters grew on the side of the MoO_2 trunk as the MoO_2 trunk was growing.

Field emission measurement was carried out in a vacuum chamber with a pressure of 4×10^{-7} Pa at room temperature. The sample with an area of 0.5 cm^2 was adhered to the surface of a stainless-steel plate served as the cathode and another stainless plate as the anode. The distance (d) between the cathode and the anode was fixed at 500 μm. Figure 3 shows the measured current density as a function of the macroscopic electric field. Defined as the electric field required at a current density of 10 $\mu A/cm^2$, the turn-on field is about 2.39 $V/\mu m$. The emission current density is up to 5.2 mA/cm^2 at an electric field of 3.8 $V/\mu m$. Such an emission current density is enough for producing sufficient brightness in flat-panel displays.[14]

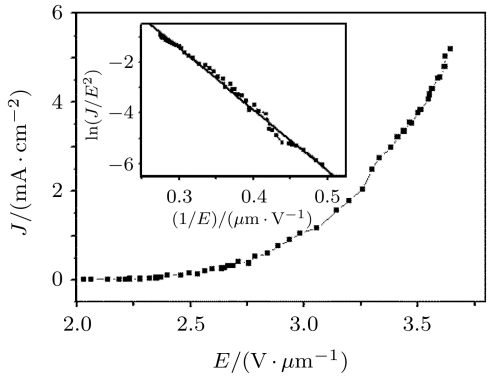


Fig.3. The field emission current density dependence of the electric field ($J-E$) for the pinaster-like MoO_2 nanoarrays. The Fowler–Nordheim plot is given in the inset.

The electron field emission is usually supposed to obey the Fowler–Nordheim (F–N) law. The relationship between the current density J and the applied field strength $E = V/d$ can be expressed as[15]

$$J = (A\beta^2 E^2/\phi)\exp(-B\phi^{3/2}/(\beta E)), \qquad (1)$$

where ϕ is the work function and β is the field enhancement factor. A and B are universal constants with the values of $1.56\times10^{-10}(\mathrm{A\cdot V^{-2}\cdot eV})$ and $6.83\times10^{9}(\mathrm{V\cdot eV^{3/2}\cdot m^{-1}})$, respectively. The inset in Fig.3 is the F–N plot ($\ln(J/E^2)$ versus $1/E$) extracted from the emission current data. The F–N plot is a straight line, indicating that the emission is governed by the electron tunnelling from the MoO_2 nanowires. Taking the work function of MoO_2 nanostructures to be 6.5 eV,[16] the enhancement factor of the pinaster-like MoO_2 nanoarrays is estimated to be 3590.

Since the length of the protruding MoO_2 nanowire is smaller than the diameter of the pinaster-like MoO_2 trunk, the pinaster-like MoO_2 nanoarrays can be considered as two-stage structures.[8] In such a model, the total enhancement factor is related to both the macro-geometry of the pinaster-like MoO_2 trunk and the microscopic structure of the protruding MoO_2 naonowires. The enhancement factor of the pinaster-like MoO_2 nanoarrays can be expressed as:

$$\beta_{\mathrm{tot}} = \beta_{\mathrm{trunk}} \times \beta_{\mathrm{wire}}, \qquad (2)$$

where β_{tot} is the total enhancement factor, β_{trunk} is the enhancement factor of the pinaster-like MoO_2 trunk, and β_{wire} that of the MoO_2 nanowires protruding from the MoO_2 trunk. According to the model given by Edgcombe and Valdré,[17] the local electric field near the tip of a cylindrical shank with high aspect ratio can be much higher than that of the applied macroscopic electric field. The ratio of the local electric field at the tip of the emitter to the macroscopic electric field, defined as the intrinsic enhancement factor, can be expressed as

$$\beta_0 = 1.2(l/r + 2.15)^{0.9}, \qquad (3)$$

where l is the length, r is the radius of the cylindrical shank and β_0 is the intrinsic enhancement factor of it. Substituting the values of l and r for the MoO_2 trunk and the MoO_2 nanowires, the intrinsic enhancement factors of the MoO_2 trunk and the MoO_2 nanowires can be calculated to be 22 and 323, respectively.

However, the enhancement factor of the arrays is affected by the spacing between the emitters because the electric field on one emitter is screened by the neighbouring emitters.[4] Nilsson *et al* have proved that the emitted current density can be optimized by tuning the density of carbon nanotubes (CNTs).[18] Taking into consideration the screening effect of the

emitters, the enhancement factor β of the arrays can be expressed as[19]

$$\beta = \gamma\beta_0 = \beta_0[1 - \exp(-2.3172s/l)], \qquad (4)$$

where γ is a parameter describing the degree of the screening effect, β_0 is the intrinsic enhancement factor of an individual emitter, and $s$is the spacing between the emitters. In this study, γ of the MoO_2 trunk arrays was estimated to be 0.49. Then the total enhancement factor of the pinaster-like MoO_2 nanoarrays was estimated to be 3574 by combining the expressions (2), (3) and (4). This value was consistent with the value 3490 extracted from the F–N plot. The γ value of 0.49 implies that the screening effect plays an important role in the actual field emission process of the pinaster-like MoO_2 nanoarrays. It can be expected that the control of the pinaster-like MoO_2 nanoarrays packing density can further improve the field emission performance of the pinaster-like MoO_2 nanoarrays.

Emission stability of the pinaster-like MoO_2 nanoarrays was studied at a fixed voltage of 1.8 kV. The emission current density was 2.8 mA/cm^2, as shown in Fig.4; Fluctuations were about $\pm$9.2% and there was no current decline during a long-time emission. This indicates that the pinaster-like MoO_2 nanoarrays are robust for field emission.

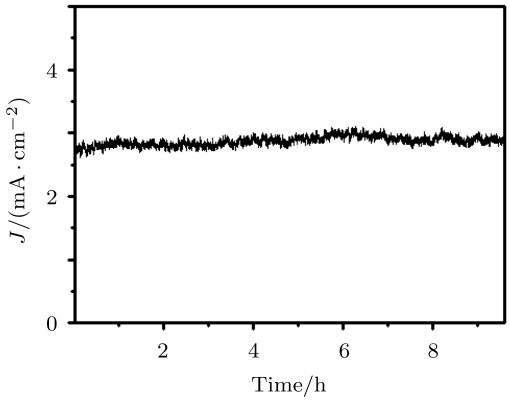


Fig.4. Stability of the emission current. The distance between the cathode and anode is 500 μm, and the applied voltage is fixed at 1.8 kV.

In summary, the pinaster-like MoO_2 nanoarrays have been synthesized via a simple thermal method. A high enhancement factor of 3590 is attributed to the two stage structures of the pinaster-like MoO_2 arrays. The current fluctuations are about 9.2% for over 9 h. Our results indicate that the pinaster-like MoO_2 nanoarrays are valuable candidates for the applications as an electron emitting source in various electronic devices.

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