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Field-emission properties of individual ZnO nanowires studied *in situ* by transmission electron microscopy

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Abstract
The field-emission properties of individual zinc oxide (ZnO) nanowires, grown by a solid–vapour phase thermal evaporation process, were studied *in situ* by transmission electron microscopy (TEM) using a home-made piezo-manipulator. The results indicate that ZnO nanowires present an outstanding field-emission property with low turn-on voltage and high emission current; the proper linearity of $1/V$–$\ln(I/V^2)$ curves basically accords with the Fowler–Nordheim model, and the dependence of the field-enhancement factor β on the distance d between the nanowire tip and its counter anode fits a linear relationship. The investigations show that ZnO nanowires show promise for potential applications as field emitters.

(Some figures in this article are in colour only in the electronic version)

Due to the promising potential of extensive applications, one of the present fields of research of one-dimensional (1D) nanomaterials is to investigate their properties arising from quantum confinement, such as electronic quantum transport and enhanced radiative recombination of carriers, which can be used for the next generation of computational devices and nanoscale lasers, respectively. The other aspect focuses on the geometric effects; for example, their high flexibility and hardness resulting from the defect-free lattice can be used to reinforce other materials, and the high aspect ratio makes them genuine candidates of electron field emission because the tip geometry and the apex structure are essential aspects of the field-emission properties [1–6]. As an oxide, ZnO exhibits a high melting point and it is quite stable under harsh environments. Therefore, ZnO-based 1D nanostructures are candidates as

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nanoscale lasers crystals and an appropriate alternative to carbon nanotubes (CNTs) for field-emission devices. So far, various types of 1D ZnO nanostructures, such as nanowires, nanorods, nanorings, nanobelts, nanocombs, and so on, have been synthesized [6–13]. In the meantime, besides the photoluminescence [14–16], magnetism [17, 18], electric transport [19–21] and mechanical properties [22–24] of 1D ZnO, field-emission properties have also been studied [25–27]. But in the previous research, the field emission of a single ZnO nanowire has not been discussed, although the field-emission currents of mass ZnO nanowires have been measured and the effects of morphology of ZnO nanostructures on the property have been investigated.

In this work, the field-emission properties of a single ZnO nanowire were studied using a piezo-manipulator by an *in situ* TEM method. The field-emission properties, including the turn-on voltage (the electric field at the voltage that produces an emission current density of 10 μA cm^{-2}), emission current, $1/V$–$\ln(I/V^2)$ curves and the dependence of field-enhancement factor β on the distance d between the nanowire tip and its counter anode were investigated. The research results suggest that ZnO nanowires show promise for potential applications as field emitters.

The ZnO nanowires were fabricated and characterized as reported in a previous paper [24]. In brief, ZnO nanowires were synthesized through pure zinc powder evaporation without a catalyst in a tubular furnace at a temperature of 650 °C. Scanning electron microscopy (SEM: Cambridge S360) and high-resolution transmission electron microscopy (HRTEM: JEOL-2010) were utilized to characterize the morphologies and structures. SEM and HRTEM researches revealed that the as-synthesized ZnO nanowires had lengths of over several tens to hundreds of micrometres and diameters ranging from 40 to 120 nm, and that they grew along [0001].

For *in situ* TEM measurement and imaging, a special TEM specimen holder was built for a JEOL 2010 FEG TEM operated under a vacuum of 10^{-7} Torr and at room temperature. An electrochemically etched tungsten needle served as the movable cathode; its opposite gold wire was the anode. The gold wire was melted into a ball shape at end. The distance between two electrodes can be precisely controlled by the piezo-manipulator. The individual ZnO nanowire was attached onto the tungsten tip by using graphite paste. The SEM image of ZnO nanowires is shown in figure 1(a) and the specimen holder with the two electrodes of the measuring device is shown in figure 1(b). The TEM beam was blanked out during the field-emission measurement and the nanowire was discharged in advance. Figures 1(c) and (d) show nanowires No. 1 and No. 2, respectively, fixed on the tungsten tip for field-emission measurement.

To study the field-emission properties and the dependence of the field-enhancement factor on interelectrode distance (between the nanowire tip and its counter electrode, denoted by d), different nanowires were adopted and field-emission measurement was performed for a serial of d-values for each nanowire. The field voltage applied on nanowires with different interelectrode distances was increased to the maximum experimental voltage value of 500 V in steps of 2 V. Because the nanowires are easily destroyed under the very high emission current density for a very close distance, it is hard to use one nanowire to get the all data at different distance range. So the data from two representative nanowires are shown. The corresponding field voltage versus field emission current (V–I) curves are shown in figures 2(a) and (b); the turn-on voltage and the maximum field-emission current (that is the emission current obtained under the maximum experimental voltage value of 500 V) of single ZnO nanowires are shown in table 1. Results indicated that the turn-on voltage decreased with decreasing the distance d, and the maximum field-emission current decreased with increasing the distance d.

The electron field-emission properties are usually analysed by using the Fowler–Nordheim (FN) model [25–27]. FN curves ($1/V$–$\ln(I/V^2)$, where I is the emission current and V is the

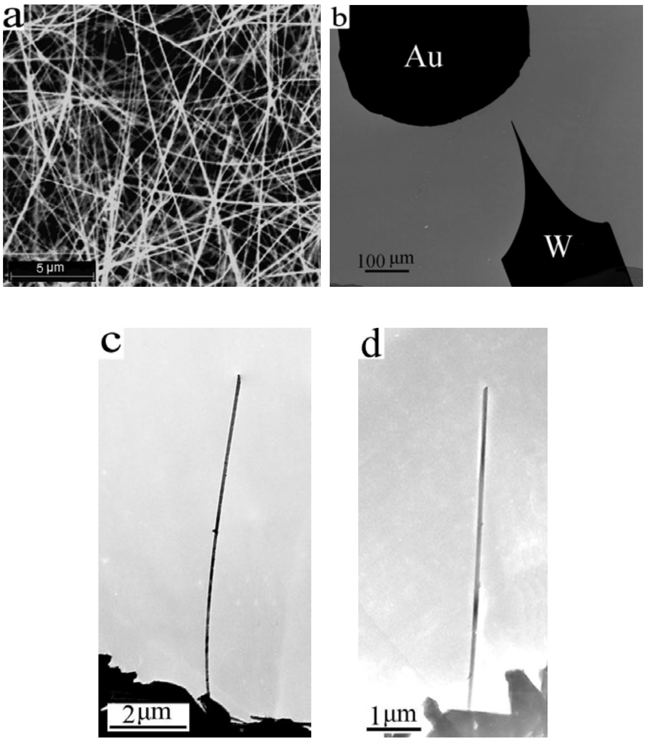

Figure 1. (a) SEM image of ZnO nanowires, (b) set-up of the *in situ* measurement with a tungsten needle as the movable cathode and gold wire as the anode, (c) TEM image of nanowire No. 1 fixed on the tungsten tip, and (d) TEM image of nanowire No. 2 fixed on the tungsten tip.

Table 1. Turn-on voltage and field-emission current at the maximum experimental voltage at different interelectrode distances.

Sample No.	Interelectrode distance, d (μm)	Turn-on voltage (V)	Field-emission current at 500 V (A)
1	1.5	298	3.69×10^{-6}
	3	304	3.29×10^{-6}
	6	312	2.85×10^{-6}
2	12	290	4.81×10^{-6}
	24	330	2.56×10^{-6}
	50	348	2.10×10^{-6}
	100	384	4.89×10^{-7}
	200	466	5.90×10^{-8}

applied voltage) are shown in figure 3. The curves can be approximately fitted to a straight line, i.e. the curves are consistent with the FN mechanism by exhibiting linear dependence.

The logarithmic equation of the FN model can be expressed as

$$\ln\left(\frac{J}{E^2}\right) = \ln\left(\frac{A}{\varphi}\right) - \frac{B\varphi^{3/2}}{E} \tag{1}$$

where J is the current density (A cm^{-2}), E is the applied field (V cm^{-1}), A and B are constants

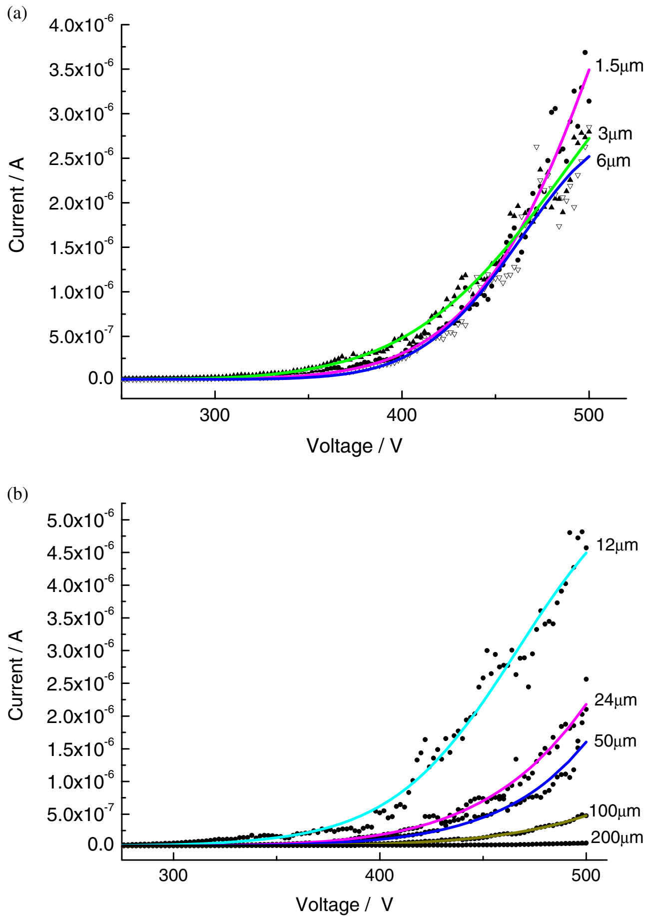

Figure 2. (a) *V–I* (field voltage versus field-emission current) curves of nanowire No. 1 and (b) *V–I* curves of nanowire No. 2 at different interelectrode distances.

($A = 1.56 \times 10^{-10}$ (A V^{-2} eV), $B = 6.83 \times 10^{3}$ (eV$^{-3/2}$ V μm^{-1})), and φ is the work function of ZnO.

The local electric field E is usually related to the applied voltage V,

$$E = \beta V/d \tag{2}$$

where d is the interelectrode distance; β quantifies the ability of amplifying the average field and is named the field-enhancement factor. Then equation (1) can be written as

$$\ln\left(\frac{I}{V^2}\right) = \ln\left(\frac{A\beta^2}{d^2\varphi}\right) - \frac{B\varphi^{3/2}d}{\beta V}. \tag{3}$$

Equation (3) reveals that the slope k of the FN curve is determined by two factors: the field-enhancement factor β and the work function φ. The expression for k is

$$k = -B\varphi^{3/2}d/\beta \tag{4}$$

where $B = 6.83 \times 10^{3}$ eV$^{-3/2}$ V μm^{-1}, $\varphi = 5.3$ eV. Slopes of FN curves with different interelectrode distances can be calculated according to the data in figure 3. The values of β

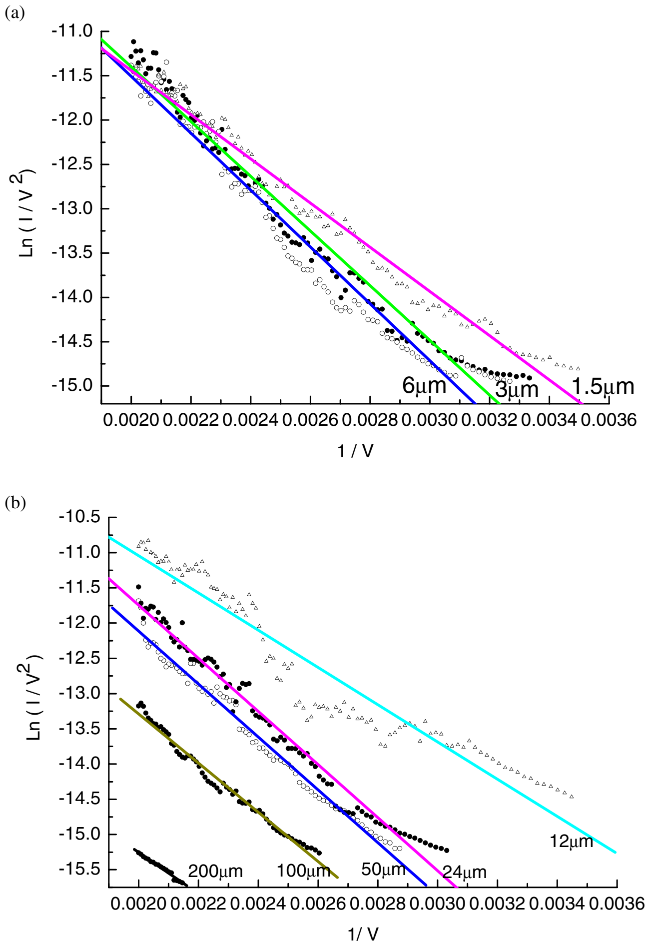

Figure 3. (a) FN ($1/V$–ln(I/V^2)) curves of nanowire No. 1 and (b) FN curves of nanowire No. 2 at different interelectrode distances.

obtained are shown in table 2. The field-enhancement factor β is measured to be several tens to several thousands, and it can be basically fitted that β increases linearly with the distance d increasing from 1.5 to 6 μm (sample No. 1) and from 12 to 200 μm (sample No. 2) respectively, as shown in figure 4.

Generally, the field-enhancement factor depends on geometry parameters, including the interelectrode distance d, wire length l, and apex radius r. In our study, the anode can be thought of as a plane electrode, and the cathode as a long needle. Through experiments and simulations, Xu *et al* [28] pointed out that such emission is different from the tip–tip or plane–plane model, but is a tip–plane emission. In their studies, the β-value of a carbon nanotube was found to be a negative power exponential of r, i.e. $\beta \propto r^{-0.5}$; the nanotube length has nearly no influence on β, and the β-value increases linearly on increasing the distance d. Comparing the experimental conditions and results, the field emission of an individual ZnO nanowire is similar to that of a carbon nanotube and accords with the tip–plane model.

In summary, ZnO nanowires were synthesized by a solid–vapour phase thermal evaporation process, and the field-emission properties of individual ZnO nanowires were

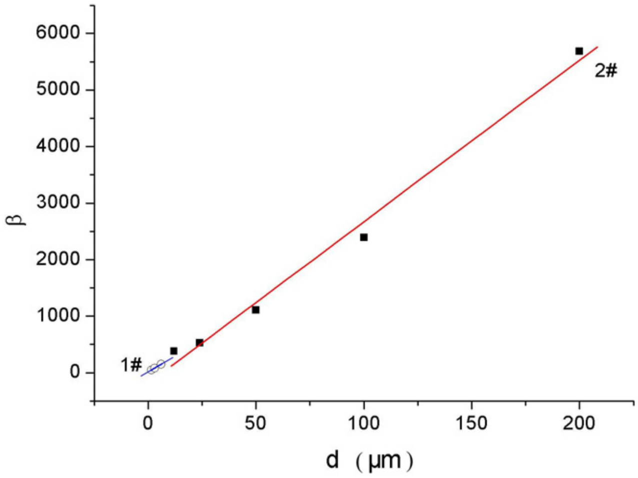

Figure 4. Curves of field-enhancement factor β versus interelectrode distance d of nanowires.

Table 2. Interelectrode distance, slope of FN curves and field-enhancement factor of ZnO nanowires.

Sample No.	Interelectrode distance, d (μm)	Slope of FN curves (k)	Field-enhancement factor (β)
1	1.5	−2585	48
	3	−3154	79
	6	−3319	150
2	12	−2642	378
	24	−3767	530
	50	−3753	1110
	100	−3489	2388
	200	−2930	5687

studied by an *in situ* TEM method using a home-made piezo-manipulator. The single ZnO nanowire presents outstanding field-emission property with low turn-on voltage and high emission current. The turn-on voltage decreases with decreasing the interelectrode distance d, and the maximum field-emission current decreases with increasing the distance. The $1/V$–$\ln(I/V^2)$ curves are consistent with the Fowler–Nordheim mechanism by exhibiting linear dependence. On the other hand, the dependence of the field-enhancement factor β on the interelectrode distance can be fitted to a linear relationship, i.e. the factor increases linearly from several tens to several thousands as the distance increases. Based on the experimental results, ZnO nanowires are likely to be potential candidates as field emitters.

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