In situ TEM probing properties of individual one-dimensional nanostructures

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Abstract: One-dimensional nanomaterials are a fundamental component of nanoscience and nanotechnology. Property measurements of individual one-dimensional nanostructures, including nanowires and nanotubes, are challenging due to their small size, which constrains the applications of the well-established testing and measurement techniques. We have developed an alternative novel approach that allows the direct measurements of the mechanical and physical properties of individual nanostructures inside high-resolution transmission electron microscopy (TEM), by which microstructures of the nanomaterials can be characterised in situ. Thus the properties of nanostructures can be directly correlated with their well-defined structures by this technique. This paper will review our progress in using in situ TEM method to measure the mechanical and field emission properties of individual nanowires and nanotubes. Mechanical resonance of zinc oxide (ZnO) nanobelt, as a new important class of nanowire, was induced by an alternating electric field. Due to the rectangular cross-section of the nanobelt, two fundamental resonance modes have been observed, corresponding to the two orthogonal transverse vibration directions, showing the versatile applications of nanobelts as nanocantilevers and nanoresonators. The elastic modulus of the ZnO nanobelts was measured to be ~52 GPa and the damping time constant of the resonance in vacuum of 10^{-8} Torr was ~1.2 ms. Field emission properties of individual carbon nanotubes have been systematically studied. The field emission behaviours have been directly linked with in situ nanotube tip morphology and their real work function. The dynamic field emission of a nanotube at mechanical resonance was also studied by in situ TEM method.

Keywords: in situ TEM; mechanical property; field emission; zinc oxide nanobelt; carbon nanotube; one-dimensional nanostructure.

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1 Introduction

It is known that the properties of nanomaterials depend strongly on their structure, size and chemical composition. To maintain and utilise the basic and technological advantages offered by the size specificity and selectivity of nanostructures, it is significant to characterise the properties of an individual nanostructure with well-defined structure. Characterising the properties of individual nanostructures is still a challenge to many existing testing and measuring techniques because of their small size, which constrains the well-established testing techniques. And the small size of nanostructures also makes their manipulation rather difficult. Thus the new methods and methodologies must be developed to quantify the properties of individual nanostructures. In recent years, one kind of special transmission electron microscopy (TEM) specimen stage with the function of scanning tunnelling microscopy (STM) was developed [1–17]. This in situ TEM method not only can provide the properties of an individual nanostructure, but also can give the microstructure through TEM analysis. It is an ideal technique for understanding the property-structure relationship of the nanostructures.

This paper reviews our recent progress in using in situ TEM technique for probing the mechanical and field emission properties of the two kinds of typical one-dimensional nanomaterials, zinc oxide (ZnO) nanobelts and carbon nanotubes.

ZnO is an important technological material. ZnO nanobelts [18–20] are single crystals with specific oriented surfaces. They have a distinct structural morphology, characterised by a rectangular cross-section and a uniform structure, which could be directly used as versatile nanocantilevers and nanoresonators in nanoelectromechanical systems (NEMS) [21]. A key phenomenon for applying nanobelts in NEMS technology is their electromechanical resonance behaviour [22]. It is essential to study the shape-dependent mechanical properties of an individual ZnO nanobelt, and an important physical quantity for cantilever applications is their elastic modulus.

The unique structure of carbon nanotubes indicates they are ideal objects that can be used for producing high field emission current density in flat panel displays. Considering the variation in diameters and lengths of the carbon nanotubes, the measured *I–V* characteristics are an averaged contribution from all of the nanotubes. Using the in situ TEM instrument we built, the field emission properties of a single carbon nanotube, including static and dynamic, have been systematically investigated [23,24].

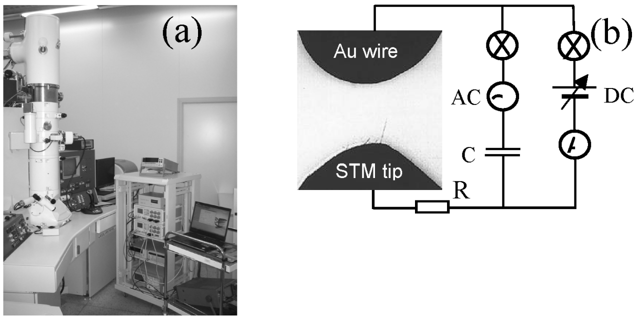
2 Experimental approach

TEM is a conventional tool for characterising the atomic-level structures of solid state materials. A novel and unique approach can be developed by integrating the structural information of a nanostructure provided by TEM with the properties measured in situ from the same nanostructure. We have built a STM mechanical unit integrated with a commercial TEM. The STM unit is responsible for manipulation and property measurements of individual nanostructures. The structural information and physical phenomenon can be observed in situ TEM.

Figure 1(a) is the picture of the combining system of STM and TEM. To carry out the in situ manipulation and property measurement of an individual wirelike nanostructure, a specimen stage for a high-resolution TEM was built for applying a voltage (AC/DC) across the nano-object and its counter electrode. An electrochemically etched tungsten needle served as the movable cathode driven by a piezo-manipulator, its opposite gold wire was the anode. Figure 1(b) is a diagram of the measurement electric circuit and the TEM image showing one end of the nano-object is electrically attached to STM tungsten tip, and the other end faces directly against its opposite gold wire. The static and dynamic properties of the individual nano-objects can be obtained by applying a controllable static and alternating electric field.

In our studies, an oscillating voltage with tunable frequency was applied on the wirelike nano-object. Mechanical resonance of the nano-object can be induced if the applied frequency matches the natural vibration frequency. So the mechanical behaviour is obtained by the frequency response of the vibration amplitude and elastic modulus of the nanostructure is achieved from its resonance frequency, geometrical parameters and mass density. For studying the field emission properties, a DC voltage was applied across the nanostructures and its counter anode, the *I–V* curve was measured and the work function at the emitter tip was obtained in situ with the assistance of an AC power supply.

Figure 1 (a) Experimental instrument of the in situ nanomanipulation and nanomeasurement, a home made STM unit is equipped on a JEOL 2010 FEG TEM. (b) Diagram of the electric circuit of property measurements



3 Mechanical properties of individual ZnO nanobelts

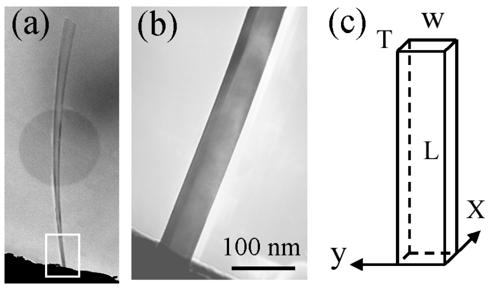
A fixed ZnO nanobelt can be regarded as a vibration cantilever clamped at one end and with another free end, as shown in Figure 2(a). Figure 2(b) is the enlarged-magnification TEM image of the nanobelt root in Figure 2(a), showing the nanobelt is a rectangular cantilever. Figure 2(c) is schematic geometrical shape of the nanobelt with length *L*, width *W*, and thickness *T*. According to the classical elasticity theory for a rectangular beam, the fundamental resonance frequency corresponding to the thickness direction (x-axis in Figure 2(c)) is

$$\nu_{xi} = \frac{\beta_i^2 T}{4\pi L^2}\sqrt{\frac{E_x}{3\rho}}, \tag{1}$$

where β_i is a constant for the ith harmonic: $\beta_1 = 1.875$ and $\beta_2 = 4.694$, E_x is the elastic modulus for the vibration along the x-axis, ρ is mass density; and the corresponding resonance frequency in the width direction (y-axis in Figure 2(c)) is given by

$$\nu_{yi} = \frac{\beta_i^2 W}{4\pi L^2}\sqrt{\frac{E_y}{3\rho}}. \tag{2}$$

Figure 2 (a) TEM image of a fixed ZnO nanobelt at mechanical resonance as induced by an oscillating voltage at $f = 0.576$ MHz. (b) TEM image recorded from the root of the nanobelt, showing the rectangular beam. (c) Schematic geometrical shape of the nanobelt

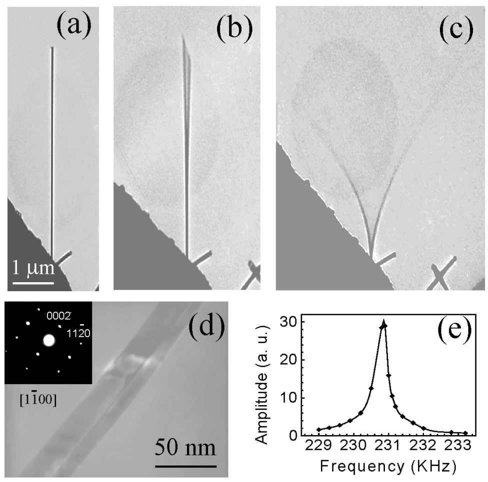


The ratio of the two fundamental frequencies is directly related to the aspect ratio of the nanobelt by $v_{y1}/v_{x1} = W/T(E_y/E_x)^{1/2}$.

Thus, the elastic modulus of a ZnO nanobelt can be obtained, based on the measured data of the fundamental resonance frequency (v_1) and the dimensional sizes (L, W and T).

A selected ZnO nanobelt at stationary is given in Figure 3(a). By changing the frequency of the applied voltage, we have found two fundamental frequencies in two orthogonal transverse vibration directions. Figure 3(b) shows a harmonic resonance with its vibration plane nearly parallel to the viewing direction, and Figure 3(c) shows the harmonic resonance with the vibration plane closely perpendicular to the viewing direction.

Figure 3 A selected ZnO nanobelt at (a) stationary, (b) the first harmonic resonance in x direction, v_{x1} = 622 kHz, and (c) the first harmonic resonance in y direction, v_{y1} = 691 kHz. (d) An enlarged image of the nanobelt and its electron diffraction pattern (inset). The projected shape of the nanobelt is apparent. (e) The FWHM of the resonance peak measured from another ZnO nanobelt. The resonance occurs at 230.9 kHz



For calculating the elastic modulus, it is critical to accurately measure the fundamental resonance frequency (v_1) and the dimensional sizes (L, W and T). Using the projected dimension measured from the TEM image (Figure 3(d)), the geometrical parameters of this nanobelt are determined to be $W = 28$ nm and $T = 19$ nm, see details in [16]. Based on the experimentally measured data, the elastic modulus of the ZnO nanobelts is calculated using equations (1) and (2). The elastic modulus of this ZnO nanobelt was measured to be ~52 GPa.

The full width at half maximum (FWHM) of the resonance peak is shown in Figure 3(e), and $\Delta v/v_1 \sim 0.2\%$. This value is independent of the vibration modes or the size of the nanobelt. To explore the intrinsic meaning of the measured $\Delta v/v_1$ value, we consider a one-dimensional harmonic oscillator with a natural frequency v_1. When a viscous (or frictional) force is acting on the particle and the force is proportional to the instantaneous speed of the particle, the damping of the vibration amplitude is given by $\exp(-t/\tau_0)$, where τ_0 is the damping time constant of the oscillator. The lifetime τ_0 is related to $\Delta v/v_1$ by following equation for $\Delta v/v_1 \ll 1$,

$$\tau_0 = [(\Delta\nu/\nu_1)\pi\nu_1/1.732]^{-1}. \quad (3)$$

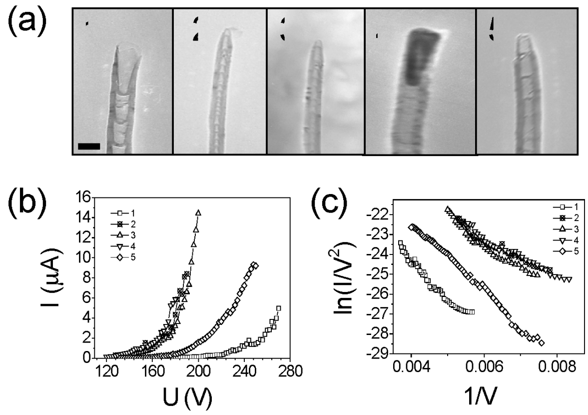
For $\Delta\nu/\nu_1 = 0.2\%$, $\nu_1 = 231$ kHz, the lifetime is $\tau_0 = 1.2$ ms. From the definition of τ_0, the viscosity (or friction) coefficient $\eta = 2M/\tau_0$, where M is the mass of the particle. Thus, the damping time constant depends on the viscosity coefficient of the nanobelt in the medium in which the measurement was carried out.

4 Field emission properties of individual carbon nanotubes

4.1 Linking field emission with in-situ emitter image and real work function

The free-standing carbon nanotubes were imaged in the TEM, which exhibit different tip structures: open end, closed end with contamination, close end with clean surface, with catalyst particle on top, and those with peeled-off caps, as indicated by numbers 1–5 in Figure 4(a), respectively. Their *I–V* curves and corresponding F-N plots are shown in Figure 4(b) and (c). The emission current increases exponentially while increasing interelectrode voltage. Their turn-on voltage is different due to the different interelectrode distance and the different field enhancement factor for the five cases [23]. A single nanotube with diameter of 31.7 nm (sample No. 2 in Figure 4(a)) can endure a current of 14.5 μA, and after some time the top surface became clean. But its turn-on field increased, which suggests that the field emission performance may be improved by the contamination and/or adsorbate on the emitter tip, although the performance is unstable.

Figure 4 (a) TEM images of emitting tips for nanotubes 1–5. Scale bar: 50 nm. (b) *I–V* curves of different nanotubes marked by 1–5 in (a). (c) Corresponding F-N plots



The F-N plot ($\ln(I/V^2)$ vs. $1/V$, where I is emission current and V is applied voltage) (see Figure 4(c)) can be approximately fitted to a straight line, in agreement to the expected result from the Fowler-Nordheim equation, which correlates the emission current with the surface potential, in agreement with that of the others [25]. In the F-N theory, the field emission current is determined by two factors: field enhancement factor β and work function ϕ, which is expressed as

$$I = KF^2/\phi\exp(-B\phi^{3/2}/F) \quad (4)$$

where $B = 6.83 \times 10^9$ V eV$^{-3/2}$ m^{-1}, K is a constant. The local electric field F is usually related to the applied voltage V as $F = \beta V/d$, where β quantifies the ability of amplifying the average field V/d, it is named as field enhancement factor. The conventional way to determine β from the measurements is to trace an F-N plot, whose slope k can be expressed as

$$k = -B\phi^{3/2} d / \beta. \tag{5}$$

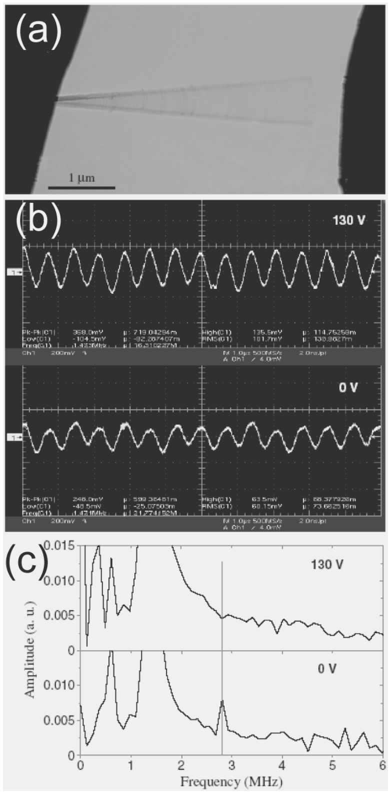
According to equation (5), if the work function is known, the field enhancement factor β can be deduced from the slope k of the F-N plot.

We focused on the case of sample Nos. 2 and 3. Although they have the same tube geometry, a large difference of field emission behaviour has been demonstrated. At the beginning, there was some amorphous carbon sticking at the tip. After several cycles of measurements, the amorphous carbon was burnt out by the emission current, and only the clean tube cap was left. For these two cases, their actual work functions at the tip were measured by in situ TEM method [26,27]. Their work functions were 4.51 eV and 4.78 eV, corresponding the sample Nos. 2 and 3, respectively. Their field enhancement factors were calculated to be β 300 and 230, respectively. This clearly showed that it is very necessary to use the actual work function in situ rather than to use a constant work function as in previous work. This is the reason why the emission performance of sample No. 3 decreases. Here, the field emission properties of individual nanostructures can be detected by directly linking the emitter structure and work function. This is a key step towards quantifying the field emission properties of an individual nano-object with well-defined structure.

4.2 Dynamic field emission of a nanotube at electromechanical resonance

The dynamic field emission of a carbon nanotube at mechanical resonance has been also studied by in-situ TEM technique. It is found that the vibration of a carbon nanotube can influence the field emission current when the nanotube approaches closely to its counter electrode. The coupling between field emission of a nanotube under a DC voltage applied longitudinal and its mechanical resonance stimulated transversely by an AC field shows that the frequency of field emission oscillating current is twice of that of the mechanical resonance. Figure 5(a) shows the resonance of a nanotube at $f = 1.473$ MHz under DC voltage $V = 130$ V. An oscilloscope was used to trace the field emission current, as shown in Figure 5(b), which indicates an AC oscillating signal at $V = 130$ V and $V = 0$ V, respectively. In practice, there is an oscillating signal component at the oscilloscope that is due to the coupling with the AC source. Thus, at $V = 130$ V, the output of the circuit current signal is composed of two parts: one from the field emission current of the nanotube, and the other from the coupling with the AC excitation source. To separate the two components, the Fourier transform of the circuit signal shown in Figure 5(b) was carried out and the results are given in Figure 5(c). At the double fundamental frequency of excitation source, $f = 2.946$ MHz, the amplitude of the total signal is distinctly different from the coupling signal, indicating that the field emission signal is an oscillating current with a frequency that is twice of the mechanical resonance frequency.

Figure 5 (a) A resonant carbon nanotube at f = 1.473 MHz. (b) the recorded circuit currents by the oscilloscope at applied dc voltage V = 130 V (above) and V = 0 (below). (c) Fourier transform analysis of the current signals presented in (b)



The in situ TEM method demonstrated here has the advantage of driving the nanotube very close to its counter electrode, and the physical environment can be designed per experimental needs, so that the oscillation component in the field emission as stimulated by the AC coupling is detectable experimentally. This method allows the observation, manipulation and measurement to be performed simultaneously, which also allows the structure and properties of individual nanotubes or nanowires to be defined, providing a powerful technique for investigating the nanoscale electro-mechanical coupling in NEMS.

5 Conclusion

The method based on in situ measurements in TEM is powerful because it can directly correlate the atomic-scale microstructure of the individual nanostructures with their properties, which provides a one-to-one correspondence in structure-property characterisation. For applications of our home-made in situ TEM instrument, the individual ZnO nanobelts and carbon nanotubes were adopted to study their mechanical and field emission properties.

The mechanical behaviour of the individual ZnO nanobelts has been characterised. The dual resonance modes with two orthogonal directions have been observed. The single crystalline, structurally controlled nanobelts could be used as a new type nanoresonator and nanocantilever with dual operation modes, which could be useful in NEMS and advanced functional nanodevices.

We have performed in-situ measurements on the field electron emission properties and work functions of individual carbon nanotube emitters. The field enhancement factors are determined by the real work function at the emitting tip. A simultaneous determination of the structure and real work function while measuring the field emission behaviour yields useful insights about the field emission characteristics of one-dimensional nanostructures. The dynamic field emission of a single carbon nanotube at mechanical resonance has been also studied by in-situ TEM technique. The oscillating field emission current could have potential applications in nanooscillating circuits, low-power loss radio frequency filter in NMES, etc.

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