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Higher-order harmonic resonances and mechanical properties of individual cadmium sulphide nanowires measured by *in situ* transmission electron microscopy

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Abstract The higher-order harmonic resonances, including second and third harmonic modes, were induced by applying alternative current signals inside a high-resolution transmission electron microscope (HRTEM), which have been used to study the mechanical properties of individual cadmium sulphide (CdS) nanowires. Young's moduli (E) and mechanical quality factors (Q) of individual CdS nanowires with diameters in the range of 50–350 nm were measured with the assistance of the mechanical resonances. The results indicate that the smooth nanowires have larger E and Q in comparison with the rough nanowires, and for the rough nanowires, E and Q increase with increasing diameters. The morphology- and size-dependent mechanical properties of CdS nanowires are directly correlated with their structure, as imaged by *in situ* TEM.

Keywords *in situ* TEM, higher-order harmonic resonances, mechanical properties nanowires

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Due to its extremely small size and enhanced physical properties, one-dimensional nanostructure materials are promising for nanoelectromechanical systems, electronics and energy conversion applications, such as high-frequency nanowire electromechanical resonators [1–3], single-atom sensitivity carbon nanotube mass sensors [4–6] and nanowire piezoelectric nanogenerater [7]. It is of significance to understand the unique mechanical properties of nanomaterials based on their morphology, size and atomic-level structure. So far, several methods for measuring the mechanical properties of nanomaterials, for example, bending test by atomic force microscope (AFM) [8,9], electrostatic pull-in approach [10], axial tensile loading [11], instrumented indentation [12] and contact-resonance AFM [13], have been developed. With the assistance of electric-induced mechanical resonance, an *in situ* transmission electron microscopy (TEM) method has been invented to directly measure the Young's modulus of individual nanotubes [14,15], nanowires [16,17] and nanobelts [18]. The most important advantage of the *in situ* TEM approach is that it allows the properties of the nano-object to be directly correlated with its structure, providing a powerful technique for investigating the structure-dependent mechanical properties of individual nano-objects [19,20].

Here, we report the morphology- and size-dependent mechanical behaviours of individual cadmium sulphide (CdS) nanowires studied by *in situ* TEM where the higher-order harmonic resonances

of individual nanowires were excited by the applied alternative current (AC) signals. With the assistance of the electric-induced mechanical resonances, Young's moduli (E) and mechanical quality factors (Q) of individual CdS nanowires have been measured, which are directly linked with their structure characterized by *in situ* TEM.

The CdS nanowires were synthesized by the chemical vapour deposition method with diameters from tens of nanometres to hundreds of nanometres, as reported elsewhere [21]. To carry out the mechanical property measurements, nanowires were attached to the tungsten scanning tunnelling microscopy (STM) tip with graphite paste. The STM tip was loaded into a home-made specimen holder, and then it was inserted inside a TEM (JEOL 2010 FEG TEM under the vacuum of 10^{-7} Torr at room temperature) [22]. The selected nanowire was driven to approach its counter electrode (Pt) by a three-directional nanomanipulator. Using an AC signal generator (Stanford Research System DS345), an oscillating voltage [$V(t) = V_{ac}\cos(2\pi ft)$] ranging from 0.1 to 10 V was applied across the CdS nanowire and its counter electrode, and the mechanical resonance was induced by tuning the frequency of the AC signal.

A stationary selected CdS nanowire is given in Fig. 1a, which can be regarded as a vibration cantilever clamped at one end. By adjusting the frequency of the applied voltage, the natural resonance was achieved at f_1 = 15.3 kHz, as shown in Fig. 1b. The enlarged TEM image (inset of Fig. 1a) indicates that the nanowire is cylindrical. The amplitude at resonance was maintained below length/10 to minimize the bending curvature, thus it fits the assumptions of the Euler–Bernoulli equation [23]. Under this condition, resonance frequency can be expressed by the following equation:

$$f_j = \frac{\beta_j^2}{8\pi L^2}\sqrt{\frac{E}{\rho}} \qquad (1)$$

where D, L, E and ρ are the diameter, length, Young's modulus and mass density of the nanowires, respectively, and β_j is a constant for the jth harmonic: β_1 = 1.875, β_2 = 4.694 and β_3 = 7.855, such that Young's modulus can be obtained from the length L and diameter D measured by *in situ* TEM. For the CdS nanowire with L = 120 μm and D = 317 nm

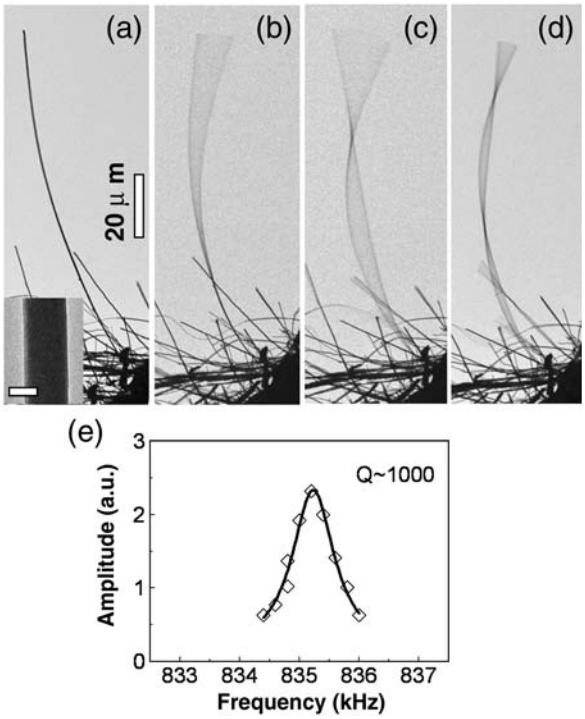

Fig. 1. (a) A stationary CdS nanowire with the length of 120 μm and diameter of 317 nm, respectively. Inset, low-magnification image shows that the nanowire has a smooth surface. Inset scale bar = 200 nm. (b) The first harmonic mode f_1 = 15.3 kHz. (c) The second harmonic mode f_2 = 91.0 kHz. (d) The third harmonic mode f_3 = 281.5 kHz. (e) The vibration amplitude *versus* frequency is fitted to a Lorentzian curve where Q ~ 1000 is measured for a smooth CdS nanowire, whose resonance occurred at 835.2 kHz.

given in Fig. 1a, E is measured as ~119 GPa. The second and third harmonic of the same nanowire were also observed, as shown in Fig. 1c and d. Their resonance frequencies are f_2 = 91.0 kHz = 5.95 f_1 and f_3 = 281.5 kHz = 18.4 f_1, respectively. They are very close to the theoretical ratios that are $f_2/f_1 = \beta_2^2/\beta_1^2$ = 6.2 and $f_3/f_1 = \beta_3^2/\beta_1^2$ =17.5, respectively [23]. The node position of the second harmonic is 0.73 L, in good agreement with the theoretical value 0.78 L. For the f_3 mode, there are two nodes, 0.45 L and 0.85 L (Fig. 1d), well fitting the theoretical rations 0.5 L and 0.87 L [23]. The consistency of the observed frequency ratios and node positions with the theoretical data are solid evidences that the true fundamental natural frequency has been found, which is crucial for this study.

The mechanical quality factor Q can be obtained from the full width at half maximum of the resonance peak, i.e. $Q = f_1/\Delta f$. Fig. 1e shows that Q is ~1000 when a resonance occurred at 835.2 kHz.

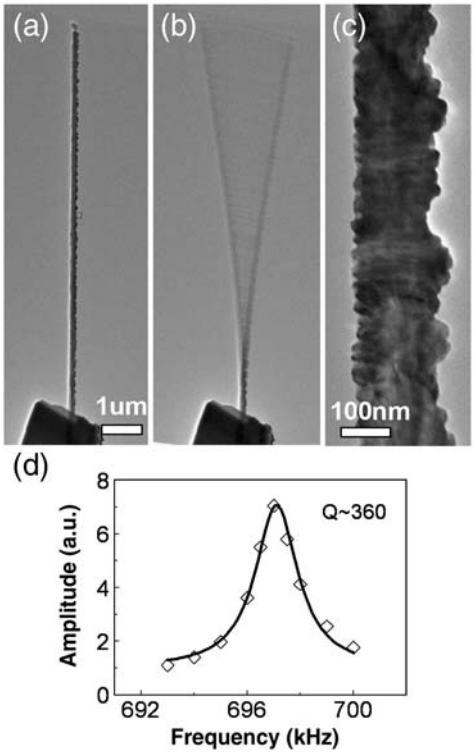

Fig. 2. A CdS nanowire at (a) the stationary and (b) the first harmonic mode. (c) A high-magnification TEM image showing the rough surface of the nanowire. (d) The vibration amplitude *versus* frequency is fitted to a Lorentzian curve. The Q is measured as ~360 for this CdS nanowire and the resonance occurred at 696.7 kHz.

Fig. 2a gives another stationary selected CdS nanowire with L = 9.5 μm and D = 159 nm. The natural resonance was excited at the frequency of 696.7 kHz, as shown in Fig. 2b. Young's modulus was measured as ~38 GPa and the quality factor Q of this nanowire is ~360, as displayed in Fig. 2d, both are smaller than those of the nanowire in Fig. 1a. The TEM image (Fig. 2c) shows that this nanowire has a rough surface, which is different from the nanowire having a smooth surface in Fig. 1a (inset).

In this study, 19 nanowires in total have been measured, whose diameters are in the range of 64–317.5 nm, including smooth nanowires and rough nanowires. The experimental results are summarized in Fig. 3. The Young's modulus E for the eight nanowires with smooth surfaces vary in the range of 95–196 GPa, and the mechanical quality factors Q vary in the range of 400–1000. For the 11 rough nanowires, the E are measured as 11–90 GPa and the Q are in the range of 100–600. As given in Fig. 3, the rough nanowires show a size-dependent Young's modulus, i.e. the rough nanowire with larger diameter tends to have

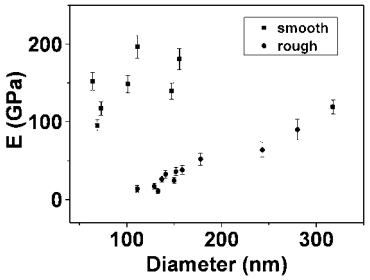

Fig. 3. E as a function of diameter. Solid rectangles, smooth nanowires with E ranging from 95 to 196 GPa. Solid circles, rough nanowires with E ranging from 11 to 90 GPa.

a higher E, and the E of smooth nanowires are larger than those of the rough nanowires. The Young's modulus of bulk CdS is about 62 GPa [24], which is equivalent to our data for the nanowires with rough surface, and the measured Young's modulus of nanowires with the smooth surface is 1.5–3 times as large as that of bulk CdS, which could be attributed to the surface effect as reported elsewhere [17].

To explore the origin of the morphology- and size-dependent mechanical behaviours of CdS nanowires, microstructure characterization of nanowires were carried out using high-resolution transmission

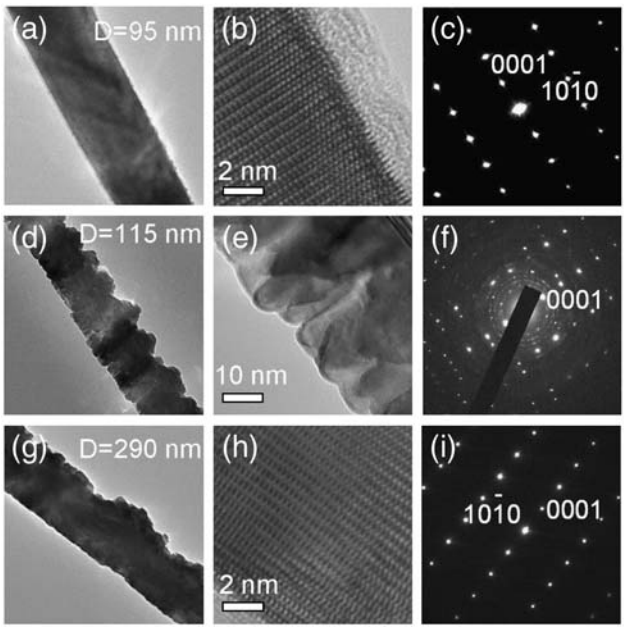

Fig. 4. (a) Low-magnification TEM image, (b) HRTEM image and (c) ED pattern of a nanowire with smooth surface growing along the [0001] direction, and its diameter is 95 nm. (d) Low-magnification TEM image, (e) HRTEM image and (f) ED pattern of a nanowire with rough surface and growth direction along [10–10], and its diameter is 115 nm. (g) Low-magnification TEM image, (h) HRTEM image and (i) ED pattern of a rough surface nanowire and growth direction along [10–10], and its diameter is 290 nm.

electron microscopy (HRTEM) images and electron diffraction (ED) patterns. Fig. 4a–c shows a low-magnification TEM image, a HRTEM image and an ED pattern, respectively, of a typical smooth surface nanowire with 95 nm in diameter and growth direction along [0001]. The HRTEM image shows its high-quality single crystal, which is also confirmed by the ED pattern recorded from the same nanowire. Fig. 4d–f shows the TEM characterization of a typical rough surface nanowire with 115 nm in diameter and growth direction along [10–10]. The HRTEM image (Fig. 4e) shows the presence of planar defects. The ED pattern (Fig. 4f) also shows the non-uniform crystal structure with polycrystalline reflection spots. Such planar defects were observed for all the nanowires with rough surfaces. For the rough nanowires with larger diameters, the crystal quality is improved and defect density is reduced, as shown in Fig. 4g–i, whose diameter is 290 nm.

Furthermore, the mechanical quality factors Q also show the morphology and size dependence. The nanowires with smooth surfaces have larger Q in comparison with the nanowires with rough surfaces, and for the rough nanowires, the nanowires with larger diameters have larger Q than those with smaller diameters. It is known that the inverse factor $1/Q$ is related to the energy dissipation, which is determined by the intrinsic properties of 'internal friction' involving surface and defect effects. Since the air damping can be neglected in TEM (10^{-7} Torr) [19], the high defect density and grain boundary 'friction' in the rough nanowires could result in much more energy dissipation.

In summary, the higher-order harmonic resonances have been observed by the excitement of AC signals inside TEM. Young's moduli and mechanical quality factor of CdS nanowires with different morphology, size and growth orientation were measured with the assistance of the electric-induced mechanical resonances. It is found that Young's moduli and mechanical quality factor are dependent on the morphology and size of the nanowires, which are directly linked with the nanowire structure obtained through *in situ* TEM. The morphology- and size-dependent mechanical properties of CdS nanowires with known structure have implications for their nanoelectromechanical applications.

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