On the bending strength of ZnO nanowires

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ABSTRACT

Compared to bulk samples, the bending strength of ZnO nanowires exhibits nearly two orders of magnitude increase and approaches their theoretical value. Statistical analysis on the scatter strength data of ZnO nanowires by using three versatile distributions has shown that, in contrast to Young's modulus, no obvious size effect was observed, and the bending strengths were insensitive to aspect ratios and flaws at the nanoscale. The reasons for this surprising tolerance behavior can be explained by the collective interaction of "flaws" in a nontraditional sense.

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Zinc oxide (ZnO) has attracted considerable research interest over the past few years due to its remarkable semiconducting, optical and piezoelectric properties and also its richest nanostructures such as nanowires, nanobelts, nanocombs and nanocages [1]. ZnO nanowires can be applied, for example, in the next-generation of integrated circuits, optoelectronic devices, and nanoelectromechanical systems. ZnO nanowires can be also served as an ideal reinforcer to develop new composites with unique properties [1−3]. All of these applications, however, require the knowledge and ability to control the mechanical behavior of ZnO nanowires. Thus, it is vital, but very frustrating inability at present, to manufacture uniform nanowires with almost the same properties [4]. In particular, the mechanical properties of ZnO nanowires such as Young's modulus and strength have remained elusive both experimentally and theoretically; and their size dependence has been one of the largest controversial issues [5−8].

According to classic fracture mechanics, the strength of a brittle material is inversely proportional to the square root of the size of critical crack-like defects that are randomly distributed in the material [9,10]. The scattered strengths are usually observed from experiment, which can be well described by a two-parameter Weibull distribution based on the weakest link principle [11]. As the size of materials (or samples) approaches micro and nanoscales, however, several principal assumptions in the classic fracture mechanics such as continuum are clearly unsuitable [12]. Also there are few rather than numerous defects in terms of the traditional definition. Recent studies on bulk ZnO have shown that there was no obvious size effect on their strengths, and a simple extrapolation of Weibull statistics to microscales was questioned [13−15].

Compared to a low strength of ~100 MPa in bulk ZnO, a nearly two orders of magnitude increase in the bending strength of ~7 GPa was obtained in ZnO nanowires, which approaches

their theoretical strength, $E/10 = 14$ GPa, with Young's modulus $E = 140$ GPa. Even so, there were still various degrees of strength scatter observed in ZnO nanowires [6]. In this letter, statistical analysis on the bending strength data of ZnO nanowires will be conducted by using three versatile distributions and an optimal distribution will be determined in terms of a minimum information criterion. With bulk ZnO as a reference, the reasons for strength tolerance will be investigated and elaborated by the collective interaction of "flaws" in a nontraditional sense.

For a set of nominally identical samples with volume V subjected to a uniaxial stress σ, the cumulative failure probability can be expressed according to Weibull statistics as

$$P(\sigma_f, V) = 1 - \exp\left[-\frac{V}{V_0}\left(\frac{\sigma_f}{\sigma_0}\right)^m\right],$$ (1)

where V_0 is a reference volume; σ_0 and m are the normalized stress and Weilbull modulus, respectively [10,11]. Normally, a simple two-parameter Weibull distribution, $P(\sigma_f) = 1 - \exp[-(\sigma_f/\sigma_0)^m]$, is used in the fitting of strength data, where a set of identical samples was tested ($V = V_0$ in Eq. (1)). However, it seems to be still unavailable at the nanoscale with current advances in instruments and techniques, and the strength data were obtained with various lengths or diameters of ZnO nanowires [6]. For simplification, let us ignore the influence of size on their strengths [16], and as shown in Fig. 1, a two-parameter Weibull distribution fits the strength data of ZnO nanowires very well with $\sigma_0 = 7.41$ GPa, and $m = 5.69$ obtained by using the maximum likelihood method.

According to Eq. (1), the strength of a brittle material decreases as its size increases, i.e., $\sigma_f \sim V^{-1/m}$. This provides us an alternative, simple method to check the feasibility of the weakest link principle and Weibull statistics [14,15]. Similar to bulk ZnO, there seems no clear size effect on the strength of ZnO nanowires, as shown in Fig. 2, in more than three

orders of magnitude, which is much larger than that in multiwalled carbon nanotubes [17]. In contrast to Young's modulus [7], the bending strength of ZnO nanowires is independent in their aspect ratios (see Fig. 3).

Although the Weibull statistics is usually suggested to be considered first, more and more evidence indicates that, for micro and nano samples, there is not a universal strength distribution [13−15, 17]. As long as none better has been found, the Weibull distribution should be considered on an equal footing with other functions such as normal, lognormal, power law, type I extreme value distributions etc [11,18]. It is known that, without special manufacture and handling, strengths of brittle materials usually exhibit symmetrical distributions. So it is not surprised that a normal distribution can be used in the fitting of strength data. However, real strength data show more or less skewed distribution rather than symmetrical one as predicted by a normal distribution and also, strength values cannot be negative. Thus, a more natural choice is a lognormal distribution.

Based on the definition of a normal distribution, a lognormal distribution is the distribution of a random variable whose logarithm is normally distributed, and its probability density function can be written in the form

$$p(\ln \sigma_f) = \frac{1}{\sqrt{2\pi}\alpha} \exp\left[-\frac{(\ln \sigma_f - \bar{\sigma})^2}{2\alpha^2}\right], \tag{2}$$

where $\bar{\sigma}$ and α are the mean and standard deviation, respectively. Relative to the additive transformation of a normal distribution, $\bar{\sigma} \pm \alpha$, the multiplicative transformation of a lognormal distribution can be expressed as, $\bar{\sigma}^* \cdot / s^*$, where $\bar{\sigma}^*$ is an estimator of the median, s^* is the multiplicative standard deviation, and the sign "$\cdot/$" indicates "times or divided by" [19]. Next, how to correctly choose an optimal strength distribution of ZnO nanowires is pivotal for us to understand their underlying failure mechanisms.

Generally, we identify an appropriate distribution of strength data using goodness-of-fit tests. However, for small sample sizes, it is usually difficult to distinguish between two functions such as Weibull and normal distributions. The likelihood ratio appears to be the most promising for use in obtaining confidence bounds. Following a similar consideration, the likelihood ratio approach can be extended to make comparisons between distributions by a minimum (or Akaike) information criterion (AIC), which links the likelihood to a distance between true and estimated distributions, and is defined as

$$\text{AIC} = -2\ln\hat{L} + 2k \ , \tag{3}$$

where $\ln\hat{L}$ is the maximum log-likelihood for a given distribution, and k is the number of parameters to be fitted [20]. Here, the likelihood of a probability density function is defined as $L = \Pi_{i=1}^{N} p(\sigma_{f,i})$, where $\sigma_{f,i}$ is the strength of the i-th sample and N is the total number of samples (or tests). Thus, the log-likelihood of a given function is $\ln L = \sum_{i=1}^{N} \ln p(\sigma_{f,i})$. The AIC represents a rough way of compensating for additional parameters and is a useful measure of the relative effectiveness of different distributions. The best distribution is that for which AIC has the smallest value [14,15]. In typical cases, model differences which would be significant at around the 5% confidence level correspond to differences in AIC values of 1.5 to 2.

Table 1 summarizes the AIC values calculated by using Weibull, normal and lognormal distributions to bulk ZnO samples with various effective volumes and ZnO nanowires. It is obvious that, in all three bulk ZnO samples, a Weibull distribution fits the data better than a normal or lognormal distribution because the difference of their AIC values is substantial [20], i.e., $\Delta\text{AIC} = \text{AIC}_{\text{ln}} - \text{AIC}_{\text{w}} > 2$. However, the difference of AIC values between normal and lognormal distributions is not large enough to distinguish a better one. In the case of ZnO

nanowires, the difference of AIC values between Weibull, normal and lognormal distributions is not large enough to distinguish the best one. Fig. 4 shows the lognormal strength distributions of ZnO bulk (medium sample in Table 1) and nanowires in a log-probability plot. Here, it is worth noting that a normal distribution is chosen as a reference because of the unphysical assumption on strength values mentioned above. In the following discussion, we will focus on Weibull and lognormal distributions.

It is important to bear in mind that an assumption was included in the statistical analysis, where the sizes of ZnO nanowire samples are not the same as those of ZnO bulks [6,14]. The influence of such an approximation on the results is very different. In terms of the implications of a lognormal distribution [19], the influence of a sample size on its strength is only one of numerous factors rather than the critical one in a Weibull distribution. Thus, the same as ZnO bulk [14,15], a lognormal distribution may provide a better description on the strength scatter of ZnO nanowires. In other words, there is a characteristic strength in ZnO nanowires such as their mean strength in Fig. 2, and its value is dependent on the collective interaction of a lot of independent of "flaws". Different from the definition in a Weibull distribution, the "flaw" here is mentioned in a nontraditional sense, which includes quantized defects, temperature, time, and load [21,22].

Recently, nanoscale Weibull statistics, a modification of classical Weibull statistics, was proposed, in which a quantized stress σ^* was introduced. The nanoscale Weibull statistics subjected to a uniaxial stress can be formulated as, $P(\sigma^*) = 1 - \exp[-n^*(\sigma^*/\sigma_0)^m]$, where n^* is an equivalent number of defects [23]. The consequence of the multiplicative interaction of these quantized defects in a lognormal distribution is equal to introducing a mean stress at a critical defect, i.e. $n^* = 1$ in nanoscale Weibull statistics. Relative to the claim that bone-like materials become insensitive to flaws at nanoscale [24], there seems to be a new kind of flaw

tolerance where the scattered strengths of ZnO nanowires are due to the collective effect of numerous factors rather than few critical flaws. It is worth noting that, however, this conclusion is obtained based on post-mortem data analysis, further studies are needed to evaluate its universality to other nanostructured materials.

In summary, the scattered strength data of ZnO bulk and nanowires were assessed by using three versatile statistical distributions. The results showed that, in terms of a minimum information criterion, the optimal strength distribution is lognormal due to the collective interaction of "flaws" in an untraditional sense. This provides a new explanation on the nature of nano-flaws and the degree of their sensitivity to strengths, and also sheds light into a novel strategy for manufacturing uniform samples of ZnO nanowires.

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Figure captions

Fig. 1. Strength distribution of ZnO nanowires in a log-log plot of $-\ln(1 - P)$ versus σ_f, where solid line is the fitting to a two-parameter Weibull distribution in Eq. (1) with $V = V_0$.

Fig. 2. Dependence of strengths on effective volumes of ZnO nanowires, where the slope of solid line is $-1/m$ with the Weibull modulus $m = 5.69$ obtained by fitting the data to a two-parameter Weibull distribution and dashed line indicates their mean strength (7.41 GPa).

Fig. 3. Strengths of ZnO nanowires versus their aspect ratios, L/d, where L and d are the length and diameter of a nanowire, respectively.

Fig. 4. Log-probability plot for the strength distributions of ZnO bulk (medium specimen in Table 1) and nanowires, where solid lines are the fitting to a lognormal distribution in Eq. (2).

Table 1. AIC values calculated by Weibull, normal and lognormal distributions, where V indicates the effective volumes of ZnO bulk or nanowires, and the difference of AIC values is defined as $\Delta\text{AIC} = \text{AIC}_{ln} - \text{AIC}_{w}$. The strength data of ZnO nanowires are from Ref. [6].

Sample	V	AIC_{w}	AIC_{n}	AIC_{ln}	ΔAIC
bulk: small	0.40 (mm^3)	272.73	268.89	268.71	−4.02
medium	5.90 (mm^3)	681.29	671.53	672.52	−8.77
Large	33.14 (mm^3)	257.60	247.28	246.60	−11.00
nanowires	0.005–1.65 (μm^3)	47.43	47.51	48.38	0.95

Fig. 1

Fig. 2

Fig. 3

Fig. 4