Torsional Stick-Slip Behavior in WS_2 Nanotubes

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We experimentally observed atomic-scale torsional stick-slip behavior in individual nanotubes of tungsten disulfide (WS_2). When an external torque is applied to a WS_2 nanotube, all its walls initially stick and twist together, until a critical torsion angle, at which the outer wall slips and twists around the inner walls, further undergoing a series of stick-slip torque oscillations. We present a theoretical model based on density-functional-based tight-binding calculations, which explains the torsional stick-slip behavior in terms of a competition between the effects of the in-plane shear stiffness of the WS_2 walls and the interwall friction arising from the atomic corrugation of the interaction between adjacent WS_2 walls.

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Nanomechanics is a current topic of intensive research, as it has been recognized that the mechanical properties of nanoscopic structures can greatly differ from those of macroscopic structures of similar composition [1]. This is often attributed to the notion that nanostructures can have fewer defects, and hence exhibit the intrinsic properties of the material, rather than those determined by defects. Another interesting aspect, which has received less attention, is the effect of internal friction on nanomechanical properties, as it is known that atomic-scale friction can have very different mechanisms from macroscopic friction [2]. For instance, stick-slip behavior, in which oscillatory friction forces arise when two surfaces slide by each other, is a common phenomenon at macroscopic scales, from violins to earthquakes, usually attributed to a difference between the static and dynamic friction coefficients, unrelated to surface corrugation [3]. On the contrary, atomic-scale stick-slip behavior, which is observed in the wearless sliding of smooth surfaces [4], is often related to the atomic corrugation of the interaction between the surfaces [5].

Torsional stick-slip behavior, in which a torque oscillates upon torsion of an object, is macroscopically observed in various systems, such as oil well drilling platforms [6], but atomic-scale torsional stick-slip behavior has not yet been reported, to the best of our knowledge. Linear stick-slip behavior has been observed in the telescoping of multiwall carbon nanotubes (MWCNTs) [7], as predicted from their registry-dependent interwall sliding friction [8]. A stepwise helical motion of cargos along MWCNTs has been recently reported, and attributed to atomic corrugation in the interwall interaction [9]. However, the torsion of MWCNTs was shown to proceed smoothly [10–12], the outer wall sliding around the inner walls with no detectable stick-slip behavior.

Here we report the first observation of atomic-scale torsional stick-slip behavior, which we found when twisting inorganic nanotubes (NTs) of tungsten disulfide (WS_2) [13,14]. We show that when an external torque is applied to a WS_2 NT, all its walls initially stick and twist together, until a critical torsion angle, at which the outer wall slips and twists around the inner walls. This transition is followed by a reproducible series of secondary stick-slip torque oscillations. We present a theoretical model using density-functional-based tight-binding (DFTB) calculations, which explains the torsional stick-slip transition and the secondary stick-slip oscillations in terms of a competition between the effects of the in-plane shear stiffness of the WS_2 layers and the interwall friction arising from the corrugation of the van der Waals (vdW) interaction between adjacent WS_2 layers. We find that although this competition may be negligible in carbon nanotubes, it becomes significant in WS_2 NTs, owing to their higher corrugation energy [15–18], narrower distribution of chiralities between the walls [19,20], and lower shear modulus [21,22]. More generally, our results exemplify how an atomic-scale mechanism of internal friction can lead to the emergence of a new nanomechanical property.

To twist the WS_2 NTs, we fabricated nanotube-pedal devices similar to those previously used to twist carbon nanotubes [11]. A scanning electron microscopy (SEM) image of one such device is shown in Fig. 1(a). The WS_2 NTs, synthesized in a fluidized bed reactor [23], were suspended in ethanol and spread on an oxidized Si substrate (1 μm oxide). The clamps and the pedal were laid down onto the ends and middle of the WS_2 NTs by electron-beam lithography, followed by deposition of Cr (5 nm) and Au (90 nm). The nanotube and pedal were then suspended by wet etching the underlying SiO_2 with HF, followed by critical-point drying from supercritical CO_2. During the experiment [shown schematically in Fig. 1(b)], we gradually twist the WS_2 NT using an atomic force microscope (AFM) to press on the pedal with the tip, and simultaneously measure the torque and torsion angle.

Figure 1(c) shows the torque τ as a function of torsion angle ϕ for a particular nanotube during several press cycles. Each τ-ϕ curve is characterized by an initial linear

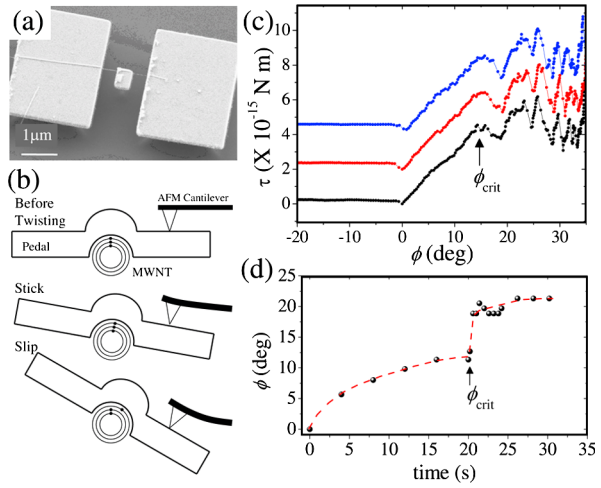

FIG. 1 (color online). (a) SEM image of a WS_2 NT-pedal device (pedal dimensions: 500×300 nm; length of suspended nanotube segments: 300 nm). (b) Schematic of the AFM experiment and stick-slip behavior. The dots are reference points to indicate the displacement of the atoms of the different layers. (c) Torque-torsion curves for several press cycles for one device (nanotube diameter $d = 22$ nm; the curves are offset for clarity). (d) Torsion angle versus time obtained from a SEM movie of a WS_2 NT ($d = 24$ nm) twisting due to charging of the pedal by the electron beam.

regime, and then a sudden drop in τ, followed by a series of torque oscillations. The curves are reproducible to fine details. A similar behavior was observed for all the eight studied WS_2 NTs [24]. This complex mechanical response, and specifically the sudden drop in torque at a particular critical angle ϕ_{crit}, could be attributed to different causes: (i) a stick-slip transition from an initial situation where all the nanotube walls twist together to a situation where the outer wall slips over the inner ones, (ii) torsional buckling of the nanotube [25–27], and (iii) elastic to plastic deformation [11,28]. The third possibility can be immediately ruled out because the curves are fully reproducible, whereas a plastic deformation should irreversibly change the mechanical response.

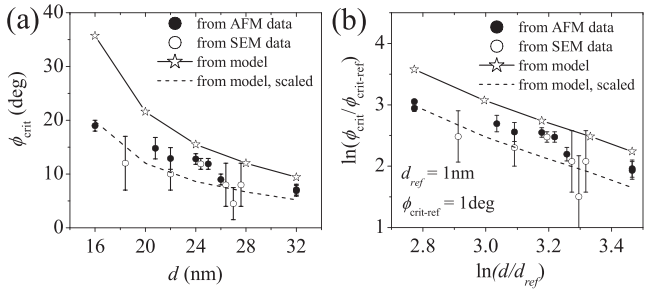

FIG. 2. (a) Diameter dependence of ϕ_{crit} from experiments (both AFM and SEM) and model. (b) Same data in a ln-ln plot showing that both experimental and theoretical ϕ_{crit} have similar scaling with d (slope: -1.9 ± 0.1).

To determine whether the critical behavior of the WS_2 NTs is due to slipping (i) or buckling (ii), we visualized the twisting process in an SEM, where the devices were actuated by the static charging of the pedal under the electron beam [24]. Movies of the pedal rotation were thus recorded for six different devices. The torsion angle ϕ as a function of time t [Fig. 1(d)] was calculated by measuring the projected length of the pedal at every frame of the movie. After the pedal is completely vertical, SEM images of the two halves of the twisted nanotubes showed a constant nanotube width [24], thereby suggesting that no torsional buckling occurred. Figure 1(d) shows that the twisting rate is not constant. Here, too, we observe a critical angle at which the pedal undergoes a sudden fast rotation.

Figure 2 shows a plot of the critical torsion angle ϕ_{crit} as a function of the nanotube diameter d, from both AFM and SEM experiments. ϕ_{crit} systematically decreases with increasing diameter. All the data fall in the same curve within experimental error, indicating that the sudden rotation observed in the SEM movies can be related to the critical torsion angle measured by AFM.

The linear portion of the τ-ϕ curves can be used to calculate a spring constant and an effective shear modulus. The shear modulus calculated assuming that all the walls twist together, as plotted in Fig. 3(a), is $G_{all} = 77 \pm 59$ GPa. Comparing this shear modulus with that expected from both DFTB calculations and Young's modulus measurements ($G \approx 80$ GPa) [16,21,22] suggests that all the walls of the nanotube are twisting together.

Beyond the critical angle ϕ_{crit}, the τ/ϕ ratio decreases to a minimum value, where the shear modulus calculated assuming that all the walls twist together no longer compares with the expected values from theory and experiment. Conversely, the shear modulus calculated assuming that only the outermost wall twists [Fig. 3(b)] is $G_{min} = 50 \pm 22$ GPa, which does lie within the range expected from theory and experiment. If we assumed that two or more walls were twisting together, then the effective shear modulus would be less than half the expected value. Based on this, and considering the relative structural perfectness of WS_2 nanotubes [22], it is fair to assume that slipping takes place between the two outermost walls, rather than

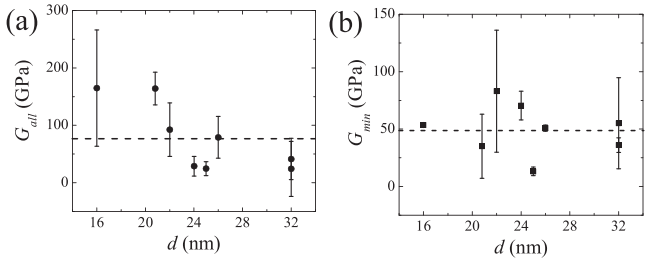

FIG. 3. (a) G_{all}, the shear modulus obtained from the linear portion of τ-ϕ curves. (b) G_{min}, the shear modulus beyond ϕ_{crit} obtained from the minimum value of τ/ϕ. The average values are indicated by the dashed lines.

between some weakly linked inner walls. These analyses suggest that the critical torsional behavior that we observe in WS_2 NTs is due to a torsional stick-slip transition with all walls twisting together below the critical angle and only the outermost wall twisting above it.

These conclusions raise three important questions: (i) Why do all the walls of the nanotube twist together initially until a critical torsion angle? (ii) Why does the critical angle decrease with increasing nanotube diameter? (iii) Why do we still observe oscillations in the torque beyond the critical angle? A recent characterization of our WS_2 NTs by aberration-corrected high-resolution transmission electron microscopy revealed that in 90%–95% of the nanotubes, the outermost wall and the next 2–3 walls all had the same chirality, either armchair or zigzag, and that the atoms of the different walls were *AB* stacked [19]. This suggests that accommodation issues are significant, and could thus force the layers to stick together when twisting, until the torsional stress becomes larger than the interwall locking interaction, and then slip over. Further accommodation issues could lead to a series of energy minima, manifesting themselves as secondary stick-slip oscillations observed beyond the critical angle.

To better understand the suggested stick-slip behavior, we developed a simple energy landscape picture based on estimations of vdW energy and torsional energy. The vdW energy cost when the outermost layer slips over the others (E_{vdW}) plus the torsional energy for the outermost layer ($E_{\mathrm{tor\text{-}1}}$) gives the total energy cost for "slipping" (E_{slip}). This is compared with the torsional energy cost for all the layers twisting together ($E_{\mathrm{tor\text{-}all}}$), which is the energy cost for "sticking" (E_{stick}). The system should stick when $E_{\mathrm{slip}} > E_{\mathrm{stick}}$, and slip when $E_{\mathrm{slip}} < E_{\mathrm{stick}}$.

The calculations of the various energies are described below. In a previous study [16] we calculated the interlayer vdW interactions in MoS_2 using DFTB calculations. Since the interlayer interaction is determined by the S atoms, a very similar interlayer interaction can be assumed for WS_2. Therefore, we estimated here the vdW energy using the data from MoS_2. As shown in [16], when one layer of MoS_2 is displaced by an amount Δa along the $\boldsymbol{a}$ axis of the unit cell, the energy change per MoS_2 unit can be approximated by

$$E(\Delta a) = \upsilon\alpha\sin^2\left(\frac{\Delta a}{a}\pi\right)\left[1 + \beta\sin^2\left(\frac{\Delta a}{a}\pi\right)\right], \quad (1)$$

where $\upsilon = 6.14 \times 10^{-23}$ cm^3 is the volume of a MoS_2 primitive unit cell, $\alpha = 35.13$ J/cm^3, and $\beta = 0.06055$.

If we consider a nanotube of length L and radius r, with N atoms along one line and P atoms along the circumference, then the total number of atoms in the tube would be NP. The nanotube is fixed at one end and twisted at the other. The atoms at the fixed end undergo no displacement, while the atoms at the twisted end undergo the maximum displacement. Because of symmetry considerations, the problem can be simplified by calculating the vdW energy for only one line of atoms along the length of the nanotube. The total vdW energy would simply be the vdW energy for one line multiplied by the number of atoms along the circumference.

If the nanotube is twisted by an angle ϕ, the displacement of the atom at the twisted end is given by $\Delta a_N = \phi r$. The displacement of the ith atom in the line would be $\Delta a_i = (i/N)\Delta a_N$. The vdW energy change for one line of atoms when the nanotube is twisted by an angle ϕ can thus be given by

$$E_{\mathrm{vdW\text{-}1}l}(\phi) = \sum_{i=0}^{N} E(\Delta a_i). \quad (2)$$

The vdW energy change between two layers of the whole nanotube would be $E_{\mathrm{vdW}}(\phi) = PE_{\mathrm{vdW\text{-}1}l}(\phi)$. The calculated $E_{\mathrm{vdW}}(\phi)$ for a nanotube of 20 nm diameter is shown in Fig. 4(a).

To calculate the torsional energies, the spring constant when one layer twists (κ_1) and spring constant when all layers twist (κ_{all}) are obtained from the theoretical shear modulus (80 GPa) using the relation $\kappa = G\pi(r_{\mathrm{out}}^4 - r_{\mathrm{in}}^4)/2L$, where r_{out} and r_{in} are the outer and inner radii, respectively. For κ_{all}, $r_{\mathrm{in}} = 6$ nm (from TEM). For κ_1, $r_{\mathrm{in}} = r_{\mathrm{out}} - \delta r$, where $\delta r = 0.62$ nm is the WS_2 interwall spacing. The torsional energies are given by $E_{\mathrm{tor\text{-}1}} = \kappa_1\phi^2/2$ and $E_{\mathrm{tor\text{-}all}} = \kappa_{\mathrm{all}}\phi^2/2$.

The stick and slip energies, $E_{\mathrm{stick}} = E_{\mathrm{tor\text{-}all}}$ and $E_{\mathrm{slip}} = E_{\mathrm{vdW}} + E_{\mathrm{tor\text{-}1}}$, are plotted in Fig. 4(a) by the black lines. It can be seen from the plot that there is a crossover from higher E_{slip} to higher E_{stick} at $\phi \approx 20°$, which would give rise to a stick-slip transition. The torque calculated from the model, $\tau(\phi) = dE_{\mathrm{min}}/d\phi$, is plotted in the inset of Fig. 4(a). The calculated torque qualitatively reproduces our experimental data. It therefore logically follows from

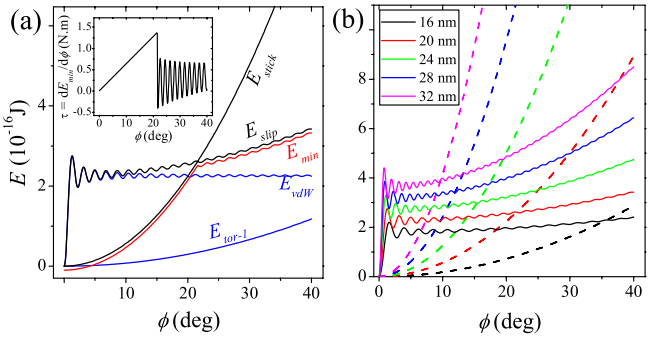

FIG. 4 (color online). Energy-based model of the torsional stick-slip behavior. (a) E_{vdW} , $E_{\mathrm{tor\text{-}1}}$, E_{stick}, E_{slip}, and the energy landscape for the system E_{min} are shown by the lines as labeled (E_{min} is slightly offset for clarity). Inset: τ-ϕ calculated from E_{min}. (b) Calculated E_{stick} (dotted lines) and E_{slip} (solid lines). Different colors are the energies for nanotubes of different diameters.

our model that the oscillations in $\tau(\phi)$ beyond ϕ_{crit} come from the undulations in $E_{\mathrm{vdW}}(\phi)$. The theoretical period of the oscillations derived from our model depends on diameter and varies from 2.3° for the 16 nm diameter nanotube to 1.2° for the 32 nm diameter nanotube. The observed torque oscillations have periods of $2 \pm 1°$, which are consistent with our model within experimental error.

The diameter dependence of ϕ_{crit} obtained from the model by repeating the energy calculations for different diameters is plotted in Fig. 2 by stars. The values of ϕ_{crit} from the model and from the data show similar diameter dependences, although the absolute values differ by nearly a factor of 2. This difference could arise from the uncertainty in the determination of the shear modulus, and also from the approximate evaluation of the interlayer vdW energy. However, the semiquantitative agreement with the experimental values from such a simple calculation strongly supports our model.

Overall, our simple energy-based model gives a qualitatively accurate description of the observed behavior. It (i) shows that there is a crossover from stick to slip motion, (ii) reproduces the diameter dependence of ϕ_{crit}, and (iii) shows that above ϕ_{crit} the $\tau(\phi)$ oscillates. By reproducing all the features of the experimental data, this model indicates that the stick-slip behavior comes from the torsional energy cost becoming larger than the vdW energy cost upon twisting.

In summary, we observed atomic-scale torsional stick-slip behavior in WS_2 NTs. The behavior consists of a stick regime where all the nanotube walls twist together, and a slip regime where the outer wall slips over the inner walls. A simple theoretical model allowed us to determine the origin of this torsional stick-slip behavior to be the competition between the vdW and torsional energies. In the slip regime, the corrugation in the vdW energy gives rise to secondary stick-slip oscillations. The observed stick-slip behavior and the oscillations in the slip regime come about due to the commensurate atomic arrangement of the WS_2 layers in a WS_2 NT and their large interlayer corrugation energy combined with their relatively small in-plane shear stiffness.

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