Nanomechanical behavior of MoS$_2$ and WS$_2$ multi-walled nanotubes and Carbon nanohorns

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Nano-objects have been investigated for drug delivery, oil detection, contaminant removal, and tribology applications. In some applications, they are subjected to friction and deformation during contact with each other and their surfaces on which they slide. Experimental studies directly comparing local and global deformation are lacking. This research performs nanoindentation (local deformation) and compression tests (global deformation) with a nanoindenter (sharp tip and flat punch, respectively) on molybdenum disulfide (MoS$_2$) multi-walled nanotubes (MWNTs), $\sim$500 nm in diameter. Hardness of the MoS$_2$ nanotube was similar to bulk and does not follow the “smaller is stronger” phenomenon as previously reported for other nano-objects. Tungsten disulfide (WS$_2$) MWNTs, $\sim$300 nm in diameter and carbon nanohorns (CNHs) 80–100 nm in diameter were of interest and also selected for compression studies. These studies aid in understanding the mechanisms involved during global deformation when nano-objects are introduced to reduce friction and wear. For compression, highest loads were required for WS$_2$ nanotubes, then MoS$_2$ nanotubes and CNHs to achieve the same displacement. This was due to the greater number of defects with the MoS$_2$ nanotubes and the flexibility of the CNHs. Repeat compression tests of nano-objects were performed showing a hardening effect for all three nano-objects.

Nano-objects have been investigated for applications that include drug delivery for cancer treatment, oil detection, contaminant removal, and tribology on the macro- to nanoscale. In some applications, they are subjected to friction and deformation during contact with each other and the surfaces on which they are used. The nano-objects can be deformed locally where they may be indented, or globally where the entire nano-object is compressed. To determine their suitability for applications, fundamental understanding of interfacial friction and wear, their mechanical properties and deformation mechanisms is needed.

In targeted drug delivery applications, Au, Fe$_2$O$_3$, polymer and SiO$_2$ nano-objects have been studied$^{1–4}$. For applications requiring chemical sensors, oxidized carbon black coated with oil detecting agents and composites of collagen and iron oxide nanoparticles have been used$^{5–8}$. In contaminant removal, magnetic shell cross-linked knedel-like nanoparticles (MSCKs) are of interest$^9$. In tribological applications on the macro- to nanoscale, a large body of data exists on nano-objects and examples of materials are given along with the various studies. Nanoparticles including Au, CNHs, Fe$_2$O$_3$, Sb, MoS$_2$ and WS$_2$; nanorods including ZnS, ZnO and AgVO$_3$; and nanotubes including MoS$_2$, WS$_2$, and CNT have been used. Studies have been carried out on the macro-scale$^{10–17}$, microscale$^{18–20}$ and nanoscale$^{15–17,21–28}$.

In many applications described, low friction and wear is desirable for efficient and sustained use. The nano-objects may come into sliding contact with each other and the surfaces in which they are used. During sliding contact, asperities present on the mating surfaces come into contact and deform, to support the load. Adhesive contacts are formed with the asperities by either physical or chemical interactions. When the surfaces move relative to each other a shear force is needed to break the adhesive bonds formed at the real area of contact. The friction measured is given as: Real area of contact is directly related to the nanomechanical properties relevant to nanoscale asperity contacts.

$$F = A_r \tau$$

where $A_r$ is the real area of contact and $\tau$ is the average shear strength of the contacts$^{20}$. Both reduction in shear strength and contact area reduces friction as well as wear. Deformation of nano-objects increases the real area of contact and causes friction and wear to increase.
For friction and wear reduction on the macro- to nanoscale, nano-objects made of MoS₂, WS₂, and graphene are of interest. In tribology, MoS₂ and WS₂ coatings and nano-objects have been used due to their ability to reduce the real area of contact between sliding surfaces and reduce friction and wear. Nanotubes made of these materials can also reduce friction and wear through rolling, sliding and exfoliation of the outer layers (peeling of layers) to form a tribofilm on the macro – to nanoscale. Nano-objects made of graphene such as CNHs have also been used for friction reduction on the macro – to nanoscale. The additional roughness provided by the nanohorns can further reduce the contact area in addition to rolling and sliding.

Understanding the mechanical behavior of MoS₂ and WS₂ MWNTs and CNHs under varying loading conditions during sliding is important for friction and wear reduction. Previous compression studies on MoS₂ and WS₂ nanoparticles have been performed using a nanomanipulator with an AFM probe. Lahouji et al. suggested rolling, sliding and exfoliation (peeling of layers) of an IF-MoS₂ nano-object, as the AFM probe was translated over it in dry conditions. These experiments were performed inside of a transmission electron microscopy (TEM) chamber. Tevet et al. also suggested rolling, sliding and exfoliation of IF-WS₂ and MoS₂ nanoparticles inside of a high resolution scanning electron microscopy (HRSEM) chamber. They were also able to show that each mechanism takes place under different loading regimes. Studies that directly compare indentation (local deformation) and compression (global deformation) have been performed on Au nanoparticles (500 nm). Similar studies on other nano-objects have not been performed. Given the importance of MoS₂ and WS₂ MWNTs and CNHs in friction and wear reduction under various loading conditions, additional studies on deformation mechanisms of these nano-objects are needed.

In this study, MoS₂ and WS₂ MWNTs and CNHs were investigated to determine their mechanical behavior. Nanoscale measurements were made to study scale effects. By using a sharp tip and a flat punch, local deformation (indentation) and global deformation (compression) behavior were studied. Repeat compression tests of all three nano-objects were performed to study nanoscale hardening.

**Methods**

Mechanical behavior under local deformation (indentation) with a sharp tip and global deformation (compression) with a flat punch were studied. MoS₂ and WS₂ MWNTs and CNHs nano-objects were selected because of their ability to reduce friction and wear. It is important to understand their mechanical behavior under different loading conditions that simulate the environments in which they may be used.

The nominal diameters of MoS₂ MWNTs were ~500 nm with lengths of 15–20 μm and for WS₂ MWNTs the nominal diameters were ~300 nm and also 15–20 μm in length. The CNHs comprised of horn shaped sheets of single-walled graphene 2–3 nm in diameter with a length of 30–50 nm. These horns, aggregate to form nanoparticles with nominal diameters of 80–100 nm.

For the determination of mechanical properties and scale effects compared to bulk, the MoS₂ MWNTs ~500 nm in diameter were selected. The large diameter of the nanotubes compared to the 100 nm radius of the sharp tip provides a flatter surface for nanoindentation compared to the other nano-objects. This allows for reduction of curvature effects. As nano-object size decreases there is less contact with the tip due to the curvature of both the tip and nano-object and this can lead to inaccurate determination of contact area. This results in errors in obtaining mechanical properties accurately. In determination of mechanical properties a displacement of 50 nm was selected. This was done to obtain well defined load-displacement curves where the contact depth does not exceed 30% of the nano-object thickness and result in substrate hardening effects.

Compression studies were also performed on the MoS₂ MWNTs to compare local and global deformation. Compression studies of WS₂ MWNTs and CNHs to observe mechanical behavior during global deformation were also performed along with repeat compression tests to study nanoscale hardening. Further details are given in the section on nanomechanical characterization for indentation and compression.

**Materials and Sample preparation.** Si (100) silicon wafers with a native oxide layer (University Wafers, Boston, MA) were ultrasonically cleaned in deionized (DI) water, followed by isopropyl alcohol (IPA) and finally acetone for 15 min each. To ensure repeatability, each experiment was performed five times and representative data are shown in the results section. Experiments were performed at room temperature (23°C) and 50–55% relative humidity for the nanotubes. To determine the hardness and elastic modulus of MoS₂ nanotube, a reduced modulus is obtained from the slope of the unloading part of the load-displacement curve. This is a function of the Young’s modules and Poisson’s ratios of diamond and MoS₂. The Young’s modulus of elasticity and Poisson’s ratio for diamond were taken as 1141 GPa and 0.07 respectively, and Poisson’s ratio for MoS₂ was taken as 0.27. The unknown Young’s modulus of MoS₂ can now be determined. Hardness is found from the ratio of the maximum load to the contact area. The data from these experiments is the average of five measurements on five different nanotubes for each load. The duration for loading and unloading was 20 s for all experiments (unless otherwise stated) to safeguard against the nanotube slipping under the indenter during more rapid and unstable loading. Topography images were also taken before and after indentation with the same tip used for indentation. All experiments were performed at room temperature (23°C) and 50–55% relative humidity.

**Nanomechanical characterization- Compression.** For compression experiments a spherical diamond tip of approximately 3.5 μm in radius was used as shown in Figure 2 (left). These experiments were only performed on the 500 nm diameter MoS₂ nanotubes. It is necessary to provide as flat a surface as possible for nanoindentation. This allows for elimination of curvature effects and more accurate determination of the contact area and mechanical properties. This was not possible with the other nano-objects due to their smaller dimensions. Hardness and elastic modulus were obtained by indenting at maximum displacement of 50 nm parallel to the sample plate. This was done to obtain well defined load-displacement curves where the contact depth does not exceed 30% of the nano-object thickness and result in substrate hardening effects.

Displacements of 100 nm were also explored and were the maximum displacements possible before the Berkovich tip penetrated the walls of the nanotube into the hollow interior which is done to explore deformation under increased deformation and friction. The Oliver and Pharr method was used to obtain the hardness and elastic modulus of MoS₂ nanotube. A reduced modulus is obtained from the slope of the unloading part of the load-displacement curve. This is a function of the Young’s moduli and Poisson’s ratios of diamond and MoS₂. The Young’s modulus of elasticity and Poisson’s ratio for diamond were taken as 1141 GPa and 0.07 respectively, and Poisson’s ratio for MoS₂ was taken as 0.27.

**Results**

Figure 1 shows representative transmission electron microscopy (TEM) micrographs of a MoS₂ nanotube with a broken edge (Top), a magnified image showing separated layers between the arrows (Left), magnified image showing broken surface layers (Center) and a magnified image of a nanotube showing stacking faults highlighted by the dashed lines (Right). Figure 1b shows agglomerated WS₂ nanotubes (Left), a magnified image with an arrow pointing to exfoliated layers (Center) and a magnified image of a nanotube showing wrinkled layers. Single-walled graphene (CNH) (Meijo University, Japan) were created as described by Iijima et al. and Kasuya et al. CNHs are spherical nano-objects made of single layers of graphene in the shape of horns. The horns agglomerate through van der Waals attraction to form the nano-object. Figure 1c shows TEM micrographs of spherical CNHs (Left) with a magnified image of the CNH (center) and a magnified image of individual nanohorns (Right). CNHs added to ethanol and MoS₂ and WS₂ nanotubes added to isopropyl alcohol (IPA) were sonicated for an hour to disperse the nano-objects. For experiments involving nano-object coated surfaces in dry conditions, several droplets of MoS₂ and WS₂ nanotubes suspended in IPA and CNHs suspended in ethanol, were deposited onto clean Si(100) substrates using a syringe. A solution concentration of 0.01 mg/ml was used. The substrate was then placed on a hot plate and heated to a temperature of about 70–80°C and left until the liquid evaporated. For the micrographs the nano-objects are deposited on a lacy carbon support (Ted Pella, Redding, CA) and then placed in a holder and observed using a TEM system (Tecnai F20, FEI, Hillsboro, OR) operated at a voltage of 200 kV with a current of 1 nA.
Mechanism. In order to understand the data presented for MoS$_2$ MWNTs and WS$_2$ MWNTs and explain mechanical behavior during deformation, it is important to provide a detailed explanation of the underlying mechanisms involved.

It is known that movement of dislocations by slip causes plastic deformation to occur. In lamellar structures as found in MoS$_2$ and WS$_2$, stacking faults that are created during material formation are accompanied by partial dislocations. Local regions in a crystal consist of layers of atoms on top of each other in a repeating pattern known as the stacking order. The first layer is designated as the 'A' layer and successive layers are given a new letter designation such as 'B' or 'C' if offset to the original layer and each other. Stacking faults result when this order is interrupted by either introduction or removal of an extra plane of atoms as shown in Figure 3. Where the fault ends within the crystal, the area separating the faulted region from the perfect crystal is a partial dislocation. Figure 3 illustrates the concept of stacking faults and partial dislocations with Frank and Shockley partials.

Frank partials are sessile and do not move by dislocation slip and prevents plastic deformation by obstructing movement of dislocations that can slide. Figure 3a shows an example, where a plane of atoms are missing within a layer of atoms with 'A to A' arrangement. The plane of atoms above and below, shift and settle into the vacant area. It is energetically unstable to have two layers of atoms with similar arrangement stacked on top of each other. To return to a more stable state, the internal arrange-

Figure 1 | TEM images of (a) MoS$_2$ MWNT (Top), a magnified image showing separated layers between the arrows (Left), magnified image showing broken surface layers (Center) and a magnified image of a nanotube showing stacking faults highlighted by the dashed lines (Right) (b) agglomerated WS$_2$ MWNTS (Left), a magnified image with an arrow pointing to exfoliated layers (Center) and a magnified image of a nanotube showing ordered layers. (c) Spherical CNHs (Left) with magnified image of CNHs (Right) (Iijima et al., 1999).
Nanomechanical characterization— compression tests using the flat punch are presented. Results for nanoindentation using a Berkovich tip and compression using a flat punch are given for MoS₂ MWNTs and only compression for WS₂ MWNTs and CNHs. For both deformation methods, representative load-displacement curves are presented. Morphological characterization, before and after deformation, is also presented using a Berkovich tip. Finally load-displacement curves for repeat characterization, before and after deformation, is also presented representative load-displacement curves are presented. Morphological characterization, before and after deformation, is also presented using a Berkovich tip. Finally load-displacement curves for repeat compression tests using the flat punch are presented.

Results and Discussion

Results for nanoindentation using a Berkovich tip and compression using a flat punch are given for MoS₂ MWNTs and only compression for WS₂ MWNTs and CNHs. For both deformation methods, representative load-displacement curves are presented. Morphological characterization, before and after deformation, is also presented using a Berkovich tip. Finally load-displacement curves for repeat compression tests using the flat punch are presented.

Nanoindentation— Nanoindentation. Indentation with a Berkovich tip was used to determine the mechanical properties of MoS₂ MWNTs. This was done using displacement control at a maximum displacement of 50 nm. Figure 4a shows a typical load-displacement curve with topography maps of the MWNTs over a 20 μm × 20 μm scan area and 2-D profiles before and after indentation. The topography maps are used to confirm the indentation of the nanotubes and that the nanotube did not slip during loading and unloading. The vertical arrows on the load-displacement curves point to pop-in events during indentation. The horizontal white arrows indicate the nanotube of interest along with the section on which the profiles were taken. The indent is highlighted by the dashed square on the “after indentation” profile and is not present on the “before indentation profile” at the same location.

Pop-ins have been observed in metallic and intermetallic materials by Göken and Kempf⁹ during initial steps of loading. They were reported to represent a sharp transition from pure elastic loading to a plastic deformation corresponding to an initial yield point. In the experiments with nanotubes pop-ins are believed to be as a result of displacement during breaking of the individual layers as well as sudden displacement through the spaces between the separated layers and already broken layers as shown in Figure 1a (Left and center). Figure 3a–b shows stacking faults where Frank and Shockley partial dislocations form at the edge of the fault. Since the Frank partials increase resistance to deformation, the breaking of the layers through plastic deformation occurs due to slip of Shockley partial dislocations which causes plastic deformation.

The hardness and Young’s modulus were found at a displacement of 50 nm normal to the basal plane and are given in Table 1. The hardness and Young’s modulus for MoS₂ MWNTs was found to be 0.6 GPa ± 0.2 GPa and 12.5 GPa ± 4 GPa respectively. Bulk MoS₂ has a similar hardness (0.6 GPa) and a Young’s modulus of 52 GPa normal to the basal plane. This was determined by Feldman⁶ based on neutron data by Wakabayashi et al.⁷ of a 2 mm thick MoS₂ crystal. The lower Young’s modulus of the MoS₂ MWNTs occurs as a result of the broken and separated layers present in the nanotube walls which provide less resistance to deformation (Figure 1a). The hardness of the MoS₂ nanotube does not follow the smaller is stronger phenomenon seen in various nano-objects made of materials including Au, Cu, Nb and Ni²⁹–⁴⁷.

In studies, for polycrystalline nano-objects, the grain sizes were smaller than those found in bulk, which leads to dislocation pile-ups and an increased density of dislocations which entangle and resists plastic deformation⁴⁸–⁵². In the case of single crystalline nano-objects, dislocation starvation occurs where the absence of dislocations in the interior of the nano-object limits plastic deformation⁵³. The thin layers that comprise the walls of the MoS₂ nanotubes are single crystalline and mechanisms associated with grain sizes are not relevant. Dislocation starvation is also not possible since stacking faults are observed in Figure 1a (Right) and both Frank and Shockley...
partial dislocations are present. In this case, separated layers, broken layers, and missing layers and Shockley dislocations decrease resistance to deformation and compete with Frank dislocations present which increase resistance to deformation, as explained previously in the mechanism section. These competing effects result in no appreciable increase in hardness.

To further understand deformation during indentation, higher displacements were also explored. Figure 4b shows indentation at a displacement close to 100 nm with a larger number of pop-ins compared to displacement of 50 nm. This is due to a greater number of defects, such as broken, separated and missing layers, encountered by the diamond tip as the layers are penetrated.

The broken and separated layers can lead to exfoliation as the layers are easier to peel apart at higher loads. In applications requiring friction and wear reduction this can be beneficial as exfoliation leads to formation of an easily sheared film which leads to lower friction and wear\cite{16,17}.

In summary, the load-displacement curves for MoS2 MWNTs revealed several pop-in effects which result from slip as the sharp tip penetrates broken layers and spaces between separated layers. No scale effects were observed. Separated layers, broken layers, and missing layers and Shockley dislocations decrease resistance to deformation and compete with Frank dislocations present which increase resistance to deformation. These competing effects result in no appreciable increase in hardness.

**Nanomechanical characterization - Compression.** Nano-objects were compressed to understand global deformation (compression) behavior and compare to local deformation (indentation). For this purpose, a tip approximately 3.5 μm in radius was used to carry out compression tests. Compression data for the MWNTs are presented first, followed by CNHs.

Figure 5 shows typical load displacement curves for compression at maximum displacements of 50, 100 and 300 nm for MoS2 and WS2 MWNTs. The vertical arrows point to some examples of pop-in events during compression of the nanotubes. These events similar to indentation are a result of breaking of the layers of the walls of the MoS2 and WS2 nanotubes where plastic deformation occurs as a result of slip of Shockley partial dislocations. In the case of MoS2 nanotubes, compression of spaces between separated layers also contributes to pop-ins. For the MoS2 MWNTs there are less pop-in events during compression compared to indentation (Figure 4). Here, the entire nanotube is compressed and there is more resistance to deformation and breaking of the layers of the nanotube walls. For WS2 MWNTs, a greater load is required for the same displacement (50 nm) as compared to MoS2 MWNTs. At a depth as low as 50 nm, hardening due to substrate effects are unlikely as the displacement is less than 30%\cite{31} of the height of the nanotubes. The higher resistance to deformation of the WS2 MWNTs, is due to fewer defects (Figure 1b), as there are no separated layers or broken layers present as in the case of MoS2 MWNTs. However, even though there are more pop-ins at higher displacements (100 nm and 300 nm) for MoS2 MWNTs the difference in load between the MoS2 and WS2 MWNTs is less as the substrate begins to influence the resistance to deformation and creates a hardening effect.

The broken layers of MoS2 MWNTs shown in Figure 1a (Center) and can lead to exfoliation as the layers come apart under increasing load. This along with already exfoliated layers (center) on WS2 MWNTs as shown in Figure 1b (Center) can lead to formation of an easily shearable film during sliding in tribological applications, which reduces friction and wear. For WS2 MWNTs, greater resistance to compression can also be beneficial for reduction of friction and wear. In instances where there is high moisture content, MoO3 and WO3 can be formed as MoS2 and WS2 become oxidized in the presence of oxygen. In these situations the film formation is interrupted as layers clump together. The water vapor present can also
condense in the defects of the crystal structure as shown in Figure 1a, b and would interrupt the easy shear of the basal planes\(^{53-55}\). Since the WS\(_2\) MWNTs offer better resistance to deformation compared to the MoS\(_2\) MWNTs, these may be more suitable for friction and wear reduction in humid conditions. In this case since the nanotube layers are not as easily exfoliated, the friction and wear reduction is as a result of reduced contact area, sliding and possible rolling\(^{16,17}\). Compression data for CNHs are now presented and compared to the MWNTs. Figure 6 shows load-displacement compression curves for CNHs for displacements of 25, 50 and 75 nm with vertical arrows pointing to pop-in events. Lower displacements were chosen for the compression due to the smaller diameter of the nanoparticles (80–100 nm). Similar to the MoS\(_2\) and WS\(_2\) MWNTs, pop-in events occur with CNHs at all three displacements. The single layer

| Mechanical Properties | MoS\(_2\) MWNTs (500 nm) | MoS\(_2\)^{10,36} (2 mm) | Graphene\(^{39,40}\) (single layer) |
|-----------------------|-------------------------|------------------------|-------------------------------|
| Young’s modulus [GPa] | 12.5 ± 4                | 52                     | 1000                          |
| Hardness [GPa]        | 0.6 ± 0.2               | 0.6                    | 950                           |

Figure 5 | Compression load displacement curves for displacements of 50 nm, 100 nm and 300 nm for MoS\(_2\) (Left) and WS\(_2\) MWNTs (Right) with the vertical arrows depicting pop-in events. Magnified images are shown inset for displacements of 50 nm to more clearly illustrate pop-in events which are a result of breaking of individual layers of the nanotubes and sudden compression of separated layers.
The nano-objects become more difficult. Tribological systems on the macro- to nanoscale as deformation can be useful in situations where repeated contacts occur in individual nanohorns as a result of their flexible nature. For tribological applications under high loads, rolling and sliding of spherical CNHs may not be possible due to their flexible nature and ability to deform easily. The individual nanohorns can still reduce friction and wear since they will not break apart easily due to the high hardness and Young’s modulus and would provide an easily shearable layer for sliding which would reduce friction and wear. In summary, MoS₂ and WS₂ MWNTs and CNHs, pop-ins are observed under low to high displacements. The mechanism for the MWNTs is different from the CNHs, where the individual walls break compared to buckling of the individual nanohorns which are flexible. This flexibility was further seen where, for a comparable displacement for all three nano-objects, CNHs required the lowest load. Further compression tests to study hardening effects of the nano-objects were also performed.

Repeat compression tests were performed at a constant displacement of 50 nm for the MoS₂ and WS₂ MWNTs and 25 nm for the CNHs. This provides an opportunity to study hardening effects on the nanoscale. Figure 7 shows load displacement curves for repeat compression for the nano-objects. For all cases higher consecutive loads are required to produce the same displacements. This depicts a hardening effect up to the loads used. The layers of the MoS₂ and WS₂ nanotube walls are pressed together and the spaces between them become smaller. As they are pressed into the substrate a higher load is required to produce the same displacement for each successive run. The vertical arrows point to examples of pop-ins as individual layers that comprise the nanotube walls break. For the CNHs, as individuals nanohorns buckle and are pressed onto each other and the substrate, further compression becomes more difficult, similar to the MWNTs. Pop-ins in this case occur due to buckling of the individual nanohorns.

In summary, all three nano-objects display pop-in effects during loading and increased resistance to deformation during repeat compression tests. CNHs required the smallest load for a displacement of 50 nm compared to the MWNTs. This is due to buckling of the individual nanohorns as a result of their flexible nature.

The increased resistance to deformation with the repeat compression can be useful in situations where repeated contacts occur in tribological systems on the macro- to nanoscale as deformation of the nano-objects becomes more difficult.

**Conclusions**

MoS₂ (500 nm in diameter) and WS₂ MWNTs (300 nm in diameter) and CNHs (80–100 nm in diameter) were investigated to determine their mechanical behavior. MoS₂ MWNTs were investigated to study scale effects and local deformation (nanoindentation) with a sharp tip. Nanoindentation was performed only on the MoS₂ MWNTs. Since decreasing nano-object size results in less contact with the tip due to the curvature of both the tip and nano-object this can lead to inaccuracies in determining contact area, consequently mechanical properties. The large diameter of the MoS₂ MWNTs provides a flatter surface for nanoindentation compared to the other nano-objects and leads to less error in determination of mechanical properties. Global deformation (compression) studies were performed on all samples including MoS₂ and WS₂ MWNTs and CNHs with a flat punch using a depth sensing nanoindenter in order to compare mechanical behavior during both types of deformation. This was carried out displacements from low to high. Hardening was investigated by compression using repeat loads.

For indentation with a sharp tip, the load-displacement curves revealed several pop-in effects which results as the sharp tip penetrates broken layers and spaces between separated layers. The hardness of the MoS₂ MWNTs was found to be similar to bulk and does not follow a smaller is stronger trend. Separated layers, broken layers, and missing layers and Shockley dislocations decrease resistance to deformation and compete with Frank dislocations present which increase resistance to deformation. This results in no appreciable change in hardness. For compression, pop-in effects from the sudden displacement of material were observed in both MWNTs during loading similar to nanoindentation for MWNTs. For CNHs pop-ins were also observed and resulted from buckling of the horns of the nanoparticle. The defected layers of MoS₂ MWNTs and the

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**Figure 6** | Compression load displacement curves for displacements of 25 nm, 50 nm and 75 nm for CNHs with the vertical arrows showing examples of pop-in events. Here pop-in events are a result from buckling of individual nanohorns.
increased resistance to deformation as a result of the layers of the nanotubes being pressed together. For the CNHs, individual horns buckle and are pressed against each other and onto the substrate making further compression more difficult.

All three nano-objects display pop-in effect during loading and increased resistance to deformation during repeat compression tests. CNHs required the smallest load for a displacement of 50 nm compared to the MWNTs. This is due to buckling of the individual nanohorns as a result of their flexible nature.

Deformation studies comparing local deformation (indentation) and global deformation (compression) on the nanoscale to examine scale effects of mechanical properties and deformation mechanisms of MoS2 MWNTs was performed. Global deformation studies on WS2 MWNTs and carbon nanohorns were also performed. These studies aid in understanding how nano-objects and materials behave during loading and unloading in tribological applications.

The knowledge gained will have far reaching effects when designing macro-to-nanoscale systems that incorporate materials with nano-dimensions for reducing friction and wear.

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**Author contributions**

D.M. performed the experiments and analyzed the data. D.M. wrote the main text and D.M. and B.B. participated equally in planning, execution, and review of the manuscript.

**Additional information**

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