

# In situ observations of graphitic staples in crumpled graphene

Alex Y.W. Lin<sup>a</sup>, Xiao-xiang Yu<sup>a</sup>, Albert Dato<sup>b</sup>, Gordon Krauss<sup>b</sup>, Laurence D. Marks<sup>a,\*</sup>

<sup>a</sup> Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208, United States

<sup>b</sup> Department of Engineering, Harvey Mudd College, Claremont, CA 91711, United States

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## ABSTRACT

Graphene is an exceptionally effective lubricant additive that performs well when crumpled rather than as flat sheets. In the literature, it has been suggested that crumpled graphene is analogous to wadding paper, and that this morphology significantly improves self-dispersion in lubricants and anti-wear behavior. We report here in situ transmission electron microscopy of crumpled graphene sliding, demonstrating that it possesses intra-sheet links and graphitic nanocrystals that provide additional mechanical stability and enable the material to reversibly deform. Crumpled graphene is closer to crumpled paper with additional staples, with the intra-sheet links and graphitic nanocrystals as graphitic staples.

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## 1. Introduction

The extraordinary mechanical and chemical properties of graphene, known for its atomically thin layer of carbon atoms arranged in a honeycomb lattice, are well understood and the number of potential applications that exploit them is rapidly increasing. For instance, graphene is one of the strongest materials measured to date [1] and is commonly used in multifunctional nanocomposites [2]. Combined with its unique electrical properties [3,4], the mechanical behavior of graphene motivates its use in components with sliding interfaces in micro- and nano-electromechanical systems [5–9]. Graphene is an attractive material for tribological applications because of its extreme mechanical properties, chemical stability [10], and low coefficient of friction [11]. Flat graphene sheets have proven effective [11,12] for wear resistance in some cases, but for many applications one wants to deliver graphene via a liquid such as a lubricant oil [8,13,14]. Flat graphene sheets tend to aggregate due to strong van der Waals attractions, while crumpled graphene, which can be produced by the substrate-free gas-phase synthesis method [15–18] and other scalable methods such as electrostatic spray deposition [19] and electrohydrodynamic deposition [20], is resistant to aggregation due to its network of ridges and vertices [21–24]. Although crumpled graphene was shown to outperform other carbon-based lubricant additives in

macroscale tribometer tests [14], the nanoscale tribological behavior is not well understood. It is generally believed that crumpled graphene behaves similarly to other crumpled thin sheets such as paper and foils [25–28], but this has not been directly verified.

## 2. Experimental details

### 2.1. Crumpled graphene synthesis

Crumpled graphene sheets were synthesized in an atmospheric-pressure microwave (2.45 GHz) plasma reactor (MKS/ASTeX AX2518). Argon gas is passed through a quartz tube (21 mm internal diameter) at a rate of 1.71 L/min through a microwave guide to generate an argon plasma at an applied microwave forward power of 250 W. A jet nebulizer was used to generate an aerosol consisting of argon gas (2 L/min) and ethanol droplets ( $2 \times 10^{-4}$  L/min). As shown in Fig. S1, a smaller alumina tube (3 mm internal diameter) that was located within the quartz tube was used to pass the aerosol directly into the plasma. Ethanol droplets rapidly evaporated in the plasma and dissociated to form solid matter. The products were rapidly cooled and then collected downstream on nylon membrane filters. The solid carbon material was collected at a rate of 2 mg/min. The material produced by this method has been shown to be pure and highly ordered graphene [15–18]. The collected graphene sheets were sonicated in ethanol for 1 min, resulting in the formation of a homogeneous black suspension.

\* Corresponding author.

E-mail address: [l-marks@northwestern.edu](mailto:l-marks@northwestern.edu) (L.D. Marks).

## 2.2. Transmission electron microscopy

Approximately 8–10 drops of the graphene solution were deposited on a fractured Si transmission electron microscopy TEM aperture grid glued on to a sharpened W needle, which allows the sample to be fitted into the AFM-TEM holder mount shown in Fig. S2. The Si fragment sat on a hot plate set to 50 °C for quick solution evaporation. The Nanofactory Instruments AFM-TEM holder, which contained a Si AFM tip with a spring constant of 5.6 N/m [29], was inserted into a 200 kV FEI Tecnai F20ST TEM at Argonne National Laboratory, which was used to characterize the tribological behavior of graphene sheets. The sample could move three-dimensionally in the holder via a piezomotor with resolutions of 0.2 Å in the x and y directions, and 0.025 Å in the z direction. In situ sliding was completed by moving the sample towards a stationary AFM tip. A TV-rate video camera was used to record the in situ sliding experiments. The graphene samples were re-examined ex situ in a 200 kV Hitachi H-8100 TEM and a 200 kV Hitachi HD-2300 STEM at Northwestern University before and after in situ TEM experiments.

## 3. Results and discussion

We demonstrate here that crumpled graphene is not simply folded paper, but significantly different, using transmission electron microscopy (TEM) to visualize friction and wear events in situ with high resolution. Starting from drop-casted graphene sheets (see Experimental details), we analyzed the nanoscale structural changes of crumpled graphene in real-time and observed in addition to the graphene sheets two types of graphitic structure: local regions with two, perhaps three folded graphene layers in a single graphene sheet, which we will refer to as intra-sheet links, and small regions with many folded layers, which we will refer to as needle-like graphitic nanocrystals. We use here and in the following sections the term “graphitic”, since the evidence indicates that they are primarily  $sp^2$  bonded regions, but we cannot exclude some  $sp^3$  bonding at edges. The graphitic nanocrystals were verified using higher-resolution imaging and electron diffraction (Fig. 1 and Figs. S3–S4, see Supplementary data).

These nanocrystals behave similarly to crosslinks in polymers, adding mechanical stability. The in situ sliding tests show that intra-sheet links within single graphene sheets changed morphology due to tensile and compressive forces. In contrast, regions that contain graphitic nanocrystals behaved like strong

crosslinks and have little or no structural change during compression, tension, or shear.

We will first discuss the larger-scale behavior, showing that it is comparable to prior reports [22,30] to cross-validate the more local in situ results which we will discuss later. Initially dispersed nanosheets with no preferential organization were collected during the in situ sliding and formed a crumpled ball, which comprised of several crumpled graphene sheets (Fig. 2 and Video S1).

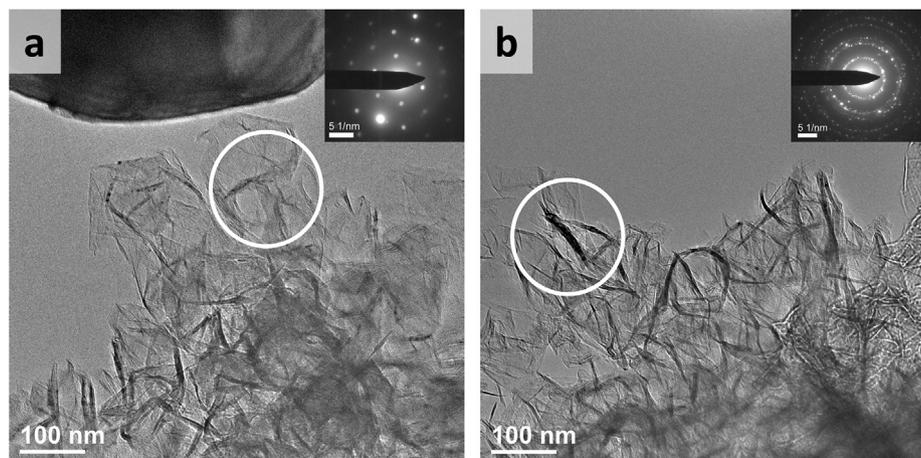
Supplementary video related to this article can be found at <https://doi.org/10.1016/j.carbon.2018.03.002>.

As sliding continued, more sheets were added to the solid. The combination of shear and compressive forces aided the formation of a spherical solid of intra-sheet links. The crumpled graphene ball, which is approximately 350–500 nm in diameter, exhibited characteristics of a non-deformable sphere and was formed from links between multiple graphene sheets. Experimentally we observed rolling in two different planes – in both the plane parallel to and the plane perpendicular to the direction of sliding. As the solid reached a size of approximately 400–500 nm in diameter, it did not add any additional graphene sheets. We also observed stick-slip in the non-deformable solid (Video S1), which can be attributed to the individual graphene intra-sheet links at the surface of the sphere. These minor intra-sheet links could be thought of as large asperities on a rounded surface. This further confirmed that the solid was constructed of many individual intra-sheet links, which were able to resist the compressive forces on the atomic force microscopy (AFM) tip by pinning these individual crumpled sheets together and preventing the individual rippled layers from unfolding back to the original state. The crumpled graphene ball's resistance to compression matched the observed behavior of crumpled thin sheets [31–34], and the ridges in the crumpled graphene were also irreversibly wadded into folds [35].

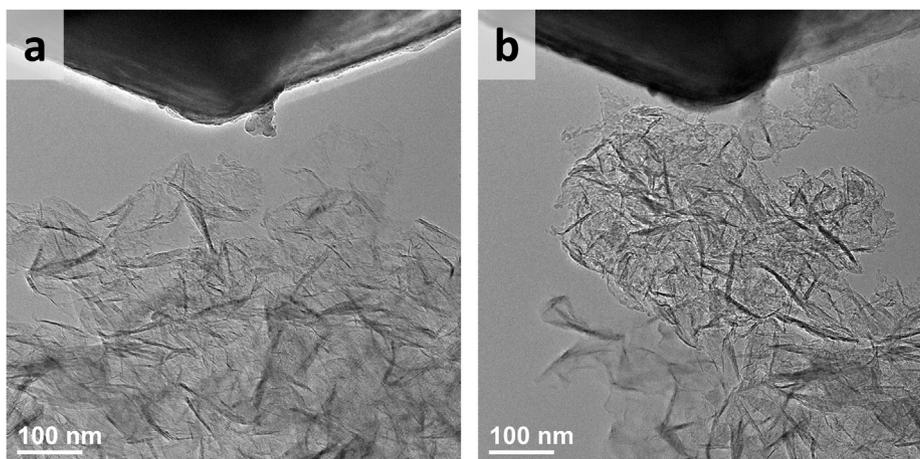
We now turn to the local processes taking place at the nanoscale, showing that localized regions within the crumpled graphene sheets changed structurally during sliding. Three examples are shown (Figs. 3–5 and Videos S2–S4).

Supplementary video related to this article can be found at <https://doi.org/10.1016/j.carbon.2018.03.002>.

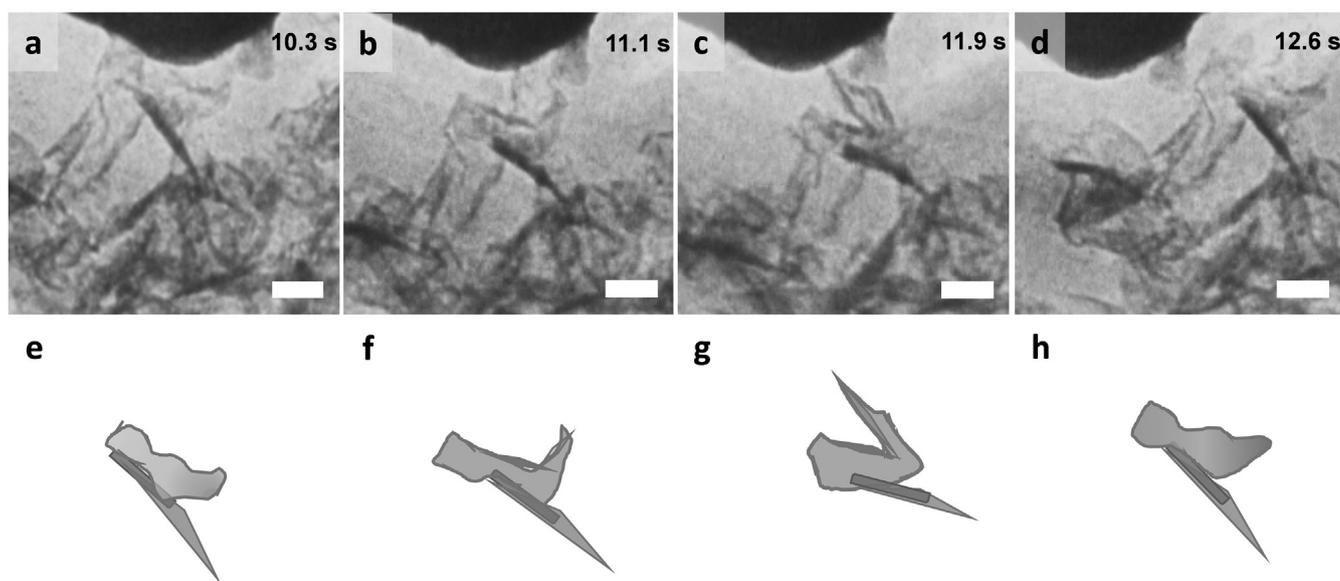
In the first example, a single crumpled graphene sheet changed structurally as it made contact with the AFM tip (Fig. 3 and Video S2). The graphene sheet folded onto itself, and then unfolded to approximately its original shape as it slid past the tip. As the graphene sheet folded, we observed that the contrast in the sheet became stronger, indicating a transformation from single layer to



**Fig. 1.** Determination of two different graphitic structures. Transmission electron diffraction patterns taken from the regions in the respective TEM images, indicated by circles, show a) intra-sheet links and b) graphitic nanocrystals.



**Fig. 2.** Formation of crumpled graphene balls. a) Prior to sliding and compression, crumpled graphene sheets have no preferential order. b) After sliding and compression, a 3D non-deformable solid with a higher density of graphitic regions, was formed.



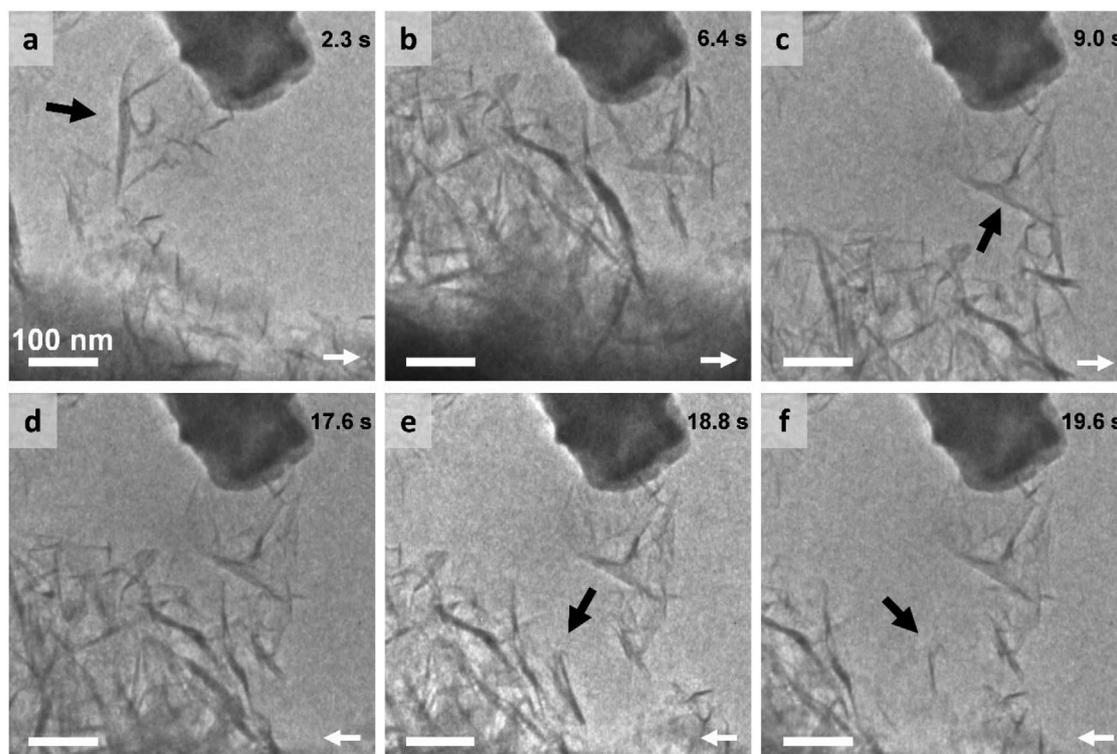
**Fig. 3.** Folding and unfolding of a single graphene sheet. a-d) TEM images extracted from Video S2 displaying that b-c) the crumpled graphene sheet supported by a graphitic nanocrystal folds as it makes contact with the AFM tip, and then d) unfolds as it passes the tip. As the graphene sheet folded, edges of the sheet were reoriented into graphitic regions. e-h) Graphical models showing the structural changes occurring as the sheet was sliding against the tip. The sample is moving from left to right in this sequence. Scale bars, 50 nm.

few-layer graphene [36]. When the graphene unfolded, we observed the opposite. By sliding this single crumpled sheet back and forth, this structural change was reproduced, suggesting that this folding and unfolding process in crumpled graphene is reversible. We note that this process is comparable to what has been shown in experiments with controlled crumpling and unfolding of graphene [24,37] and previous TEM observations of single layer regions and few-layer regions such as folded edges of graphene sheets [15,36].

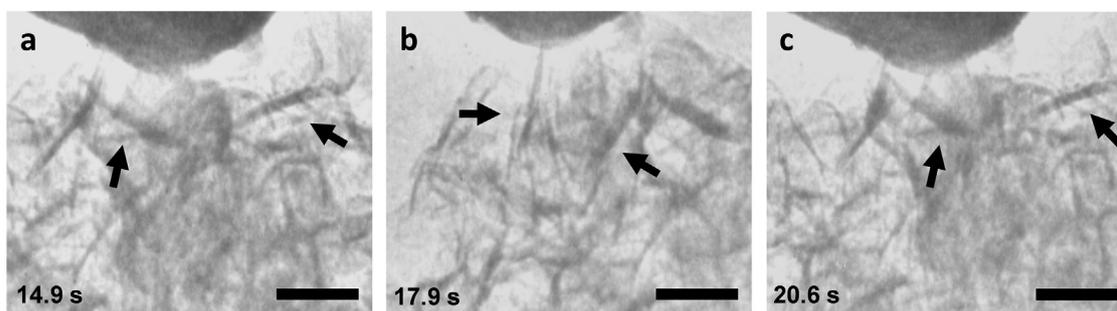
In the second example, we see folding and unfolding occurring in suspended graphene sheets (Fig. 4 and Video S3). In some of the graphitic needle-like regions near the tip we observed changes in contrast. Initially, some of the intra-sheet links in the graphene were darker, but became lighter as the sample was slid to the right of the tip (Fig. 4a–b). As the graphene sheet pivoted around the tip, the contrast weakened. However, as the substrate was retracted from the tip, the contrast in the structure became stronger (Fig. 4c).

This points to the minor changes in the thickness of the edge of the graphene sheet during sliding, and the graphitic nanocrystals moving in and out of strong diffraction conditions as they tilt when the sample was moved. The folding and unfolding was more pronounced in the suspended graphene sheet, which was located between the aggregate attached to the tip and the graphene sheets that were secured to the Si substrate. As the sample slid past the tip, we see the folded graphene sheets, depicted by the strong contrast regions, unfold and also stretch in the direction that the substrate was traveling (Fig. 4e–f). In this example, we also saw that many of the smaller localized graphitic nanocrystals did not change during the folding and unfolding, consistent with the observations from the previous example.

In the third example (Fig. 5 and Video S4), two needle-like nanocrystals, which formed the edges of a graphene sheet, were moving as the sample was sliding. The graphene sheet supported by the two needle-like graphitic nanocrystals collapsed as they



**Fig. 4.** Mechanical behavior of graphitic nanocrystals and intra-sheet links. TEM images extracted from Video S3 show that a-c) as the sample is moving to the right, graphitic nanocrystals, indicated by the black arrows in a) and c), have minimal changes in contrast under this sliding condition. This suggests that there are no significant structural changes except for some minimal rotation about the tip. d-f) As the sample moved to the left, a suspended intra-sheet link, indicated by the black arrows, almost unfolded completely. The localized intra-sheet link, which appeared very dark in e), almost completely vanished in f). White arrows indicate the sample's direction of travel. The sample was retracted approximately 200 nm between b) and c), prior to traveling from right to left in d) and f).



**Fig. 5.** Rotation of graphitic nanocrystals during sliding. a-c) Needle-like graphitic nanocrystals, indicated by arrows, acted as support for the graphene sheets. The nanocrystals converged as the sample slid toward the tip, and returned to their original configuration as the sample passed the tip. The interaction between the graphitic nanocrystals and the AFM tip collapsed the crumpled sheet. The sample is travelling from left to right in this sequence. Scale bars, 100 nm.

moved closer together, and returned to its original configuration as the nanocrystals moved apart. This structural change was reversible. As the graphitic nanocrystals were in contact with the tip, we also observed changes in the contrast within the structure, suggesting that nanocrystals were rotating and tilting as they came in contact with the tip. This observation provides further evidence that both intra-sheet links and graphitic nanocrystals add rigidity to the graphene sheets.

The intra-sheet links that formed at crumpled regions can be compared to pivot points that facilitate the folding and unfolding of individual graphene sheets. During the folding and unfolding process (Video S2), intra-sheet links, which corresponded to the edges of the sheet, began bending the sheet onto itself. Eventually, the sheet collapsed as it passed the tip. As the graphene sheet moved

farther away from the tip, the fold was relaxed and the crumpled sheet returned to the unfolded state, albeit with slight changes in morphology. Note that the graphitic nanocrystals supporting the graphene sheet mostly maintained their structure during sliding; however, we discerned a slight change in position as the graphene sheet folded and unfolded. This is the result of the reorientation of graphitic nanocrystals in the electron beam when the force was aligned longitudinally to the direction of atomic planes, allowing them to move (Fig. S5). The change in TEM image contrast of the graphitic nanocrystal is not an indication of morphological change but rather a reorientation in the electron beam (Figs. S5b–c), as the nanocrystal did not vanish as previously observed in intra-sheet links (Fig. 4e–f). The nanocrystals returned to their original positions relative to the graphene sheet, after the entire sheet slid past

the tip and unfolded. From these observations, we find that the intra-sheet links formed by the crumpled regions are more elastic, but the graphitic nanocrystals are more rigid as they do not change structurally.

The self-collapsing graphene sheets exhibited minimal or no strain hardening, in contrast to what was previously observed in crumpled graphene balls [22]. By comparing the amount of deflection of the cantilever tips in both cases (Figs. S6–S7 and Videos S5–S6), the two modes of deformation, compression and shear, exhibited similar adhesion behavior (see Supplementary data).

Supplementary video related to this article can be found at <https://doi.org/10.1016/j.carbon.2018.03.002>.

In densely packed solids such as crumpled paper balls or crumpled foils, the folds and crumples impart resistance to small compressive and shear forces [25,32,34,35,38,39]. One can “smooth out” the crumples by applying tensile forces to the edges of the sheet (Video S7). The experimentally observed folding and unfolding behavior of the crumpled graphene is similar to smoothing out crumpled paper, but there are inconsistencies, as previously suggested in molecular dynamics simulations [21]. Each individual graphene sheet has intrinsic intra-sheet links located where the crumples were formed. These ‘minor’ intra-sheet links allowed the sheets to fold and unfold when they were in contact with the AFM tip. In addition to this there is rigidity in the needle-like graphitic nanocrystals. While intra-sheet links with two to three folded layers of graphene exhibited elastic behavior, the graphitic nanocrystals are more rigid as they do not readily change. In most cases, the sliding imparts a force parallel to the sliding direction, limiting unfolding as the bending stiffness along that direction (graphitic plane direction) is high. When the applied force is longitudinal to the atomic plane, then nanocrystals reorient in the electron beam via tilt and rotation, resulting in changes in image contrast.

Supplementary video related to this article can be found at <https://doi.org/10.1016/j.carbon.2018.03.002>.

#### 4. Conclusions

In summary, we report that the substrate-free gas-phase synthesis method is capable of producing aggregation-resistant crumpled graphene that contains intra-sheet links and graphitic nanocrystals. These graphitic structures behaved similarly to staples in crumpled graphene as they increased the rigidity and structural stability of graphene sheets, as revealed by in situ sliding experiments in the TEM. We have demonstrated that direct observations using in situ TEM is a powerful experimental approach for elucidating the nanoscale mechanical behavior of crumpled graphene. Additionally, graphitic staples in crumpled graphene could be used as a model system to tune the mechanical properties of other thin nanomaterials for tribological applications.

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#### Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.carbon.2018.03.002>.

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