

# In situ observations of graphitic staples in crumpled graphene

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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.

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## 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 fiction 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).

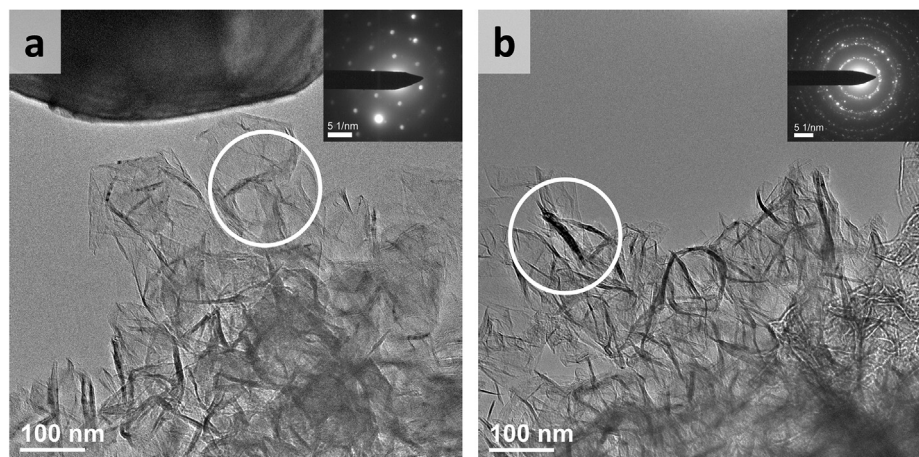
Supplementary video related to this article can be found at <https://doi.org/10.1016/j.carbon.2018.03.002>.

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.

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