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Wrinkle networks in exfoliated multilayer graphene and other layered materials

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ABSTRACT

We describe a method to obtain networks of wrinkles in multilayer graphene flakes (and other layered materials) by thermal contraction of the underlying PDMS substrate they are deposited on. The exfoliated flakes on PDMS are dipped into liquid nitrogen and after removal networks of wrinkles are found. The density of wrinkles can be controlled to some degree by sequential dipping into liquid nitrogen. Atomic force microscopy shows that wrinkles form preferentially along the armchair direction of the graphene lattice in such multilayer graphene platelets. Raman spectra show that the interlayer coupling at a wrinkle in multilayer graphene differs from, and is weaker than, that in undeformed regions. High resolution transmission electron microscopy measurements show that the interlayer distance increases in strained regions, which results in the interlayer coupling being decreased in particular regions of the wrinkles in these multilayer graphenes.

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1. Introduction

It has been observed that when materials sizes are reduced to micro- and nano-meter scales, anomalous stress-strain behaviors such as static and dynamic negative compressibility emerge [1,2]. In particular, two-dimensional (2D) materials, such as graphene, MoS₂, and WSe₂, have been reported to show unusual physical and chemical properties under stress and strain [3–9]. Due to the layered nature of 2D materials, wrinkles can be formed by applying uniaxial or biaxial stress and are known to significantly alter the materials' properties [10], for example, previous studies have shown that giant pseudomagnetic fields can be realized on strained

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graphene [11,12] and that optical absorption and photoluminescence properties in MoS_2 and other layered semiconductor materials can be tuned by strain [13,14]. Understanding how strain affects graphene's electronic and optical properties is important for science and also for technological applications. For instance, in wearable electronics, tailoring of wrinkle structures has been reported to enhance the fatigue strength of the material [15]. Thus, "straintronics" or strain-based electronics where electronic properties are modified by strain engineering has emerged as a new area of research in this field [3–5,9,16]. Creating or designing wrinkles can be potentially used to create controlled strain in the material and also allows to systematically study the mechanical behavior of wrinkled graphene.

When graphene films are exfoliated from graphite, wrinkles can be created by localized stress [4,17,18], which perturbs the crystal lattice of graphene [4]. Wrinkles are often found on exfoliated samples, but are also common in chemical vapor deposition (CVD)grown graphene both after cooling down and during transfer to other substrates [6,19,20]. Previous studies have shown that





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graphene wrinkles can be generated in a controlled way to make nanoelectromechanical systems and for creating patterned graphene nanostructures [20,21]. Wrinkles have also been studied in other 2D materials including hexagonal boron nitride (h-BN), transition metal dichalcogenides (TMDCs), silicene, monochalcogenide monolayers [22,23], and on multi-layers/superlattices of heterostructures. Although there have been some studies of wrinkling in 2D materials, such as high anisotropy in wrinkled h-BN [24], and band structure change in wrinkled MoS₂ [25], there is still much to explore, both in the creation of wrinkles and in elucidating the effect of wrinkles on material properties.

We report here an efficient method for creating wrinkles on multilayer graphene and other layered materials. Due to the large thermal expansion coefficient difference, bi-axial compression can be applied to multilayer graphene supported on a PDMS substrate during "shock" cooling in liquid nitrogen to generate wrinkles within a few seconds. Different from parallel wrinkles generated by uniaxial compression, biaxial compression can generate wrinkle networks containing junctions. Our wrinkles were studied by atomic force microscopy (AFM) and Raman spectroscopy. Hydrogen plasma etching and AFM characterization results indicated that such wrinkles are preferentially generated along the armchair direction. Raman spectroscopy showed that the 2D band is more sensitive to wrinkles than the G band; the 2D⁻ peak increases while the 2D⁺ peak decreases on top of a wrinkle, suggesting that interlayer coupling could be weaker on a wrinkle in multilayer graphene. It is likely that this thermal shock method will work for many and perhaps any other 2D materials, such as GaS, MoS₂, and WSe₂.

2. Results and discussion

Fig. 1 describes the preparation of a 'wrinkle network' in multilayer graphene flakes; more details can be found in the Supporting Information (Figs. S1–S3). Multilayer graphene (MLG) flakes were exfoliated onto a PDMS substrate and then immersed into liquid nitrogen. Due to the large volumetric thermal expansion coefficient of PDMS (9.6×10^{-4} /°C) [26], the substrate shrinks significantly as temperature is decreased from room temperature to 77 K. It was found that this contraction gave rise to biaxial compression of the MLG flakes and led to the formation of wrinkles.

As shown in Fig. 1f, the wrinkles are in the form a network. Sections of this network are straight and oriented along certain angles with respect to, e.g., the armchair direction in the MLG flake. In most cases, three wrinkles (the linear sections) join at a junction with an angle of ~120° relative to each other, indicating that the wrinkles are not generated in random directions but are influenced by the crystal orientation of the MLG flakes. Although the MLG flakes were subjected to an isotropic biaxial stress from the shrinking PDMS substrate, the stress is uniaxial on each single wrinkle. Biaxial strain is found at the center of spherical bubble structures [27]. This particular type of wrinkle network has not been so far reported on chemical vapor deposited graphene (to the best of our knowledge), presumably because CVD graphene is typically a single layer, whereas in our case, the flakes are relatively thick multilayer graphene. In addition to exfoliated MLG flakes from bulk graphite crystal, we also tested multilayer CVD graphene samples both on nickel substrates that the MLG CVD samples were grown on, and after transferring onto PDMS films, by dipping into liquid nitrogen. Wrinkle network structures were observed on both types of MLG CVD samples. However, the orientation of wrinkles on CVD graphene is "more random" when compared to that on exfoliated MLG flakes, as can be seen in Fig. S4. This could be because the CVD multilayer graphene is "already wrinkled" to some extent as a result of the interfacial compressive stress that occurs when cooling the Ni growth substrate with multilayer graphene on it, from high temperature to room temperature. Further wrinkling is then "driven" by dipping into liquid nitrogen. Wrinkle networks have been reported on exfoliated multilaver h-BN flakes on a SiO₂/Si substrate after successive annealing and cooling [24], indicating that a similar mechanism for release of biaxial stress might be operative, since the crystal structure of h-BN is very close to that of graphite. Others have reported making wrinkles on thin metal films [28,29], in which different wrinkle patterns were generated on a metal film by heating PDMS to 110 °C and then cooling down to room temperature. The random orientation of the wrinkles was explained to be due to the non-crystalline nature of the metal film.

Interestingly, when we dipped monolayer graphene flakes on PDMS substrates into liquid nitrogen, we observed no wrinkles, whereas wrinkle structures were found on bilayer graphene flakes (Fig. S5). Thus, we have focused on multilayer flakes to study wrinkle formation. As shown in Fig. S6a, MLG flakes were relatively



Fig. 1. Preparation of wrinkles in multilayer graphene by fast-cooling method. (a) and (d) Schematic of side view and top view of multilayer graphene transferred on a PDMS substrate. (b) Graphene/PDMS film dipped into liquid nitrogen. (c) Uniform biaxial compression applied on multilayer graphene flakes when PDMS is dropped into liquid nitrogen; (e) and (f) are schematic and optical images of the wrinkle network in multilayer graphene obtained through fast-cooling of the PDMS/multilayer graphene. (A colour version of this figure can be viewed online.)

flat after they were exfoliated onto ~2-mm thick PDMS and only a few wrinkles were observed. Many more wrinkles formed after dipping the PDMS into liquid nitrogen for 5 s and warming back to room temperature. The first "freeze-thaw" created a certain density of wrinkles (Fig. S6b), and after repeating this process 2 to 4 times in liquid nitrogen, the density of wrinkles increased (Figs. S6c and S6d). After dipping into liquid nitrogen five times, no further changes in wrinkle density were observed by optical microscopy. The PDMS substrate shrinks when it is dipped into liquid nitrogen and expands when it is withdrawn. The MLG flakes, in contrast, given the difference in thermal coefficient of expansion of the two materials, are not expected to deform simultaneously with PDMS during shrinking and expanding, thus giving rise to localized stress, to generate wrinkles. When repeatedly immersing the PDMS/MLG flakes into liquid nitrogen, further thermal stressing happens, and this was found to increase the density of wrinkling on the same flake. The wrinkle density also depends on the thickness of graphene flakes with increased density of wrinkles for thinner flakes (Fig. S7). A high cooling rate favored wrinkle formation, and wrinkle networks were difficult to generate if the cooling was "slow"; more experimental results are presented in Fig. S8.

During cooling, at some temperature or range of temperatures, the PDMS becomes so rigid and its "surface characteristics change so dramatically" that the MLG flakes "de-adhere" from the PDMS surface (Fig. S9). Evidently, this deadhesion ("de-pinning") happens after significant compressive stress has driven wrinkle network formation in the MLG flakes. When the PDMS is warmed back to room temperature, it seems the flakes either do not "re-adhere" at all, or they re-adhere once the PDMS becomes sufficiently "liquidlike" again that they can "re-attach". We note that the glass transition temperature of PDMS is roughly 147 K and the melting temperature is 233 K. Thus, the PDMS, a highly viscoelastic polymer at room temperature, is "frozen" and very rigid, at 77 K, and is likely very rigid well before reaching 77 K. We think it very likely that the mechanical properties of the substrate (PDMS) change so remarkably, going from very soft and "sticky" to hard and "not sticky", that compressive stress is applied while "sticky" enough and remaining in close mechanical connection with the MLG flakes. But, clearly based on our observation that MLG flakes have evidently deadhered during cooling, when the PDMS is heated back up, there is not an equivalent tensile stress during warming, as there was a compressive stress during cooling.

This fast-cooling method also generated wrinkles in GaS, MoS₂, and WSe₂ flakes that were exfoliated onto a PDMS film substrate (Fig. 2), and can thus be generalized to prepare wrinkle networks in any 2D material. Compared with the wrinkle networks observed in polymer films as reported in one study [30], the wrinkles in layered crystals show special orientation, which may be closely related to the interlayer stacking modes and crystallographic orientation. We note that we did not observe a "wrinkle-to-fold" transition on MLG flakes, as shown in TEM results below (Fig. 5a); such a transition has

been reported in "wrinkling" of polymer films [30].

Since the wrinkles are not generated in random directions in the MLG flakes, we asked if there is a relationship between the graphene lattice and the orientation of wrinkles. We (i) used atomic resolution AFM to directly examine the wrinkles and (ii) etched the surface of MLG flakes by hydrogen plasma followed by AFM imaging to determine the orientation of wrinkles. Hydrogen plasma has been reported to anisotropically etch graphene and graphite, which allows determining their crystal orientations [31]. Hexagonal pits on the graphite surface after H₂ plasma etching with all the edges along the zigzag direction have been reported [31]. Thus, wrinkle directions could be assigned if similar types of hexagonal pits were generated in wrinkled MLG flakes.

Fig. 3 presents results of AFM measurement of MLG wrinkles. After 4 h of hydrogen plasma etching, hexagonal pits were seen in the AFM image; the edges of the pits are straight and the angle at each corner is 120°, indicating that the MLG flakes are single crystals. Three wrinkles merge at a junction forming a "Y" shape and the angle between wrinkles is also 120°. The direction of wrinkles is found to be perpendicular to the (zigzag) edges of the etch pits, which means that the wrinkles are oriented along the armchair direction. By 'decorating' exfoliated h-BN flakes containing wrinkle networks with self-assembled octadecylphosphonic acid (OPA) molecules, previous studies show that the h-BN wrinkles also ran along the armchair directions [24,32]. The height (h)and width (w) of the wrinkle in Fig. 3a (marked by the yellow dashed line) are 36.5 nm and 231 nm, with a h/w ratio of 15.8%. This ratio differs depending on flake thickness and the stress applied to the MLG flakes. We found that the h/w ratio is in the range from 7% to 23% (Supporting Information, Fig. S10) for the set of exfoliated MLG flakes (all having different thicknesses) that we studied.

As an independent measure of the direction of wrinkles, atomic resolution AFM was done. Fig. 3c presents an AFM image of a wrinkle in a MLG flake similar to the one shown in Fig. 3a. The red and yellow square regions in Fig. 3c were scanned at atomic resolution and the images obtained on one side of the wrinkle and on the flat area are shown in Fig. 3d and e, respectively. Both images show the same lattice structure and that these wrinkles are oriented along the armchair direction. The observations in these two regions are thus consistent with results from hydrogen plasma etching experiment described above. To the best of our knowledge, this is the first direct observation on the atomic scale of wrinkle orientation (direction) in MLG flakes.

Raman spectroscopy has been used to study the number of graphene layers, stacking order and defect types, as well as strain in graphene [33–36]. The two dominant Raman bands in graphene, MLG, and graphite are the G and 2D bands and both peaks are sensitive to strain. The strain dependence of these two bands for graphene under uniaxial or biaxial stress has been discussed [37–39]. Raman mapping has been used to detect strain, grain boundaries, and defects in graphene [27,40]. We did Raman



Fig. 2. Optical images of wrinkle networks generated on flakes of GaS (a), MoS₂ (b), and WSe₂ (c). The flakes were first exfoliated on PDMS and wrinkles were generated by dipping the sample on PDMS into liquid nitrogen. (A colour version of this figure can be viewed online.)



Fig. 3. AFM characterization of wrinkles in exfoliated MLG flakes. (a) AFM image of MLG flake wrinkles. The MLG flake was slightly etched by H₂ plasma and from the hexagonal etch pit edges (oriented along zig-zag directions), the direction of wrinkles can be determined to be along the armchair direction. (b) Height profile of one wrinkle in (a) (marked by dashed line). (c) AFM image of another MLG flake wrinkle, which is similar to the one in (a). (d) and (e) are atomic resolution AFM images of the MLG flake surface obtained at the red and yellow areas in (c). The hexagonal atomic structures of the surface of this MLG flake are illustrated by red and yellow networks in (d) and (e). (A colour version of this figure can be viewed online.)

mapping to investigate the structural changes (such as strain, interlayer interaction) in wrinkled MLG flakes. In Fig. 4a, a Raman mapping image of the G band is presented. The position of the G peak (centered at 1581 cm^{-1}) when scanned in the interior of a

wrinkle or at a wrinkle junction was identical to that in the flat, unwrinkled areas. The 2D mode of single layer graphene has only one peak, but it splits into four peaks in bilayer graphene [41]. As the layer number increases, the 2D band can be fitted to two



Fig. 4. Raman characterization of several wrinkles in MLG flakes. (a) Raman mapping image of the G band. (b) and (c) Raman mapping images of the $2D^-$ and $2D^+$ bands; the intensity of the $2D^-$ on a wrinkle is higher than in the flat area, while the intensity of the $2D^+$ band on a wrinkle is lower than on the flat area. (d) and (e) Raman spectra of G and 2D bands measured at the flat area, on top of the wrinkle, and at the wrinkle junction. The position of the G peak is almost the same for the three different regions. However, for the $2D^-$ and $2D^+$ bands, both the relative intensity and peak half-widths are different for the flat and wrinkled regions. (A colour version of this figure can be viewed online.)

Lorentzians $(2D^{-} \text{ and } 2D^{+})$ centered at 2684 cm⁻¹ and 2723 cm⁻¹ for undoped and unstrained samples [42,43], respectively. As shown in Fig. 4b and c, the intensity of the 2D⁻ band on the wrinkle is higher whereas the intensity of the 2D⁺ band on the wrinkle is much weaker than that from the flat areas. We collected Raman spectra at different positions including a flat area, on top of a wrinkle and at the center of a wrinkle junction (see Fig. 4d and e). The G peak is identically at 1581 cm^{-1} for the three spectra collected at these positions, consistent with the mapping result discussed above. The 2D band is different, as shown in the Raman image. In Fig. 4e, the intensity of the 2D⁻ band increases from the flat area to the wrinkled area, with the highest intensity at the wrinkle junction, while the intensity of the 2D⁺ band decreases on the wrinkled regions. The intensity ratios of $I(\bar{2}_D)/I(\bar{2}_D)$ in the flat regions, on top of a wrinkle and at the wrinkle junction are 31.5%, 47.2% and 56.6%, respectively, for this particular set of wrinkles and wrinkle junction. No D peak was detected on both flat or wrinkled areas, so it seems that if C-C bonds are being broken during wrinkle formation, they must be a very small fraction of the overall structure

While both the G and 2D bands are sensitive to strain and doping, it is possible to identify and separate the spectral shifts induced by the two effects. It has been observed that in the presence of compressive or tensile strain, the ratio of $\Delta \omega_{2D} / \Delta \omega_{G}$ is in the 2.02-2.44 range [36,39]. In our previous work, we have described strain-induced Raman shifts and oscillation in Raman intensity on graphene bubbles [27]. In the present case, we did not detect any obvious strain-induced shift on wrinkles and the positions of both G and 2D peaks on a wrinkle are almost the same as on flat graphene. It is noted here that the Raman spectrum is an average signal which depends on the spot size of the laser ($0.5 \,\mu m$ in diameter), whereas the influence of strain is only in a narrow area (around a few nanometers, see further remarks below), which means that strain-induced shift may not be very obvious if the strain is only localized in a small percentage of the total area covered by the laser spot. Fig. 5 show the transmission electron microscope (TEM) cross-sectional images of one MLG wrinkle, where the strain zone is localized only in a small area in the middle (1-2 nm) in Fig. 5b and d. From the spectra measured at different areas on the sample, we find that the peak widths are larger on a wrinkle and wrinkle junction when compared to the surrounding flat regions, indicating that the detected Raman spectrum was from a mixture of flat graphene and strained graphene. The 2D band is sensitive to interlaver coupling [44,45]. For randomly stacked graphene sheets, the 2D band is a single peak because the interaction between the basal planes is weak enough that the splitting in π electron dispersion energies does not occur [46]. As the degree of graphitization increases, the 2D band splits into two components $(2D^{-} \text{ and } 2D^{+})$, accompanied by an increase in intensity of $2D^{+}$, indicating that the interlayer coupling is stronger [46]. Compared to the flat area, the relative intensity of the 2D⁺ band decreases on a wrinkle, suggesting a weakening of interlayer coupling in these regions.

Raman spectra measured over the flat regions on wrinkled MLG flakes are similar to that acquired on a freshly cleaved graphite, which shows that the flat area is made from AB-stacked graphene layers, whereas, in the wrinkled regions, the AB stacking sequence is perhaps not maintained [47,48]. The Raman results are consistent with high-resolution TEM (HRTEM) measurements, from which it was found that the interlayer distance increased from 0.33 nm in flat regions to 0.41 nm in the obviously strained region of the wrinkle. This significantly larger interlayer separation weakens the interlayer coupling.

We propose a model to understand the Raman spectral features of wrinkled MLG flakes, as shown in Fig. 5c. The wrinkle structure is chosen to be similar to the one measured by AFM (Fig. 3b), consisting of three curved surfaces as identified from the crosssectional view of the wrinkle. We use four-layer graphene as an example and assume that the strain is localized only at the curved areas marked in red (Fig. 5c). In a layered material, a deformed zone can be viewed in the form of twin boundaries [18]. In order to ensure AB-stacked crystalline structure in the flat region, the



Fig. 5. Typical TEM cross-sectional image and schematic image of a wrinkle in a MLG flake. (a) Low magnification TEM image and (b) and (d) are high-resolution images of the wrinkle corner. The strained region is at the middle part in (b) and (d), which is marked by white dashed lines. (c) Schematic image of a wrinkle in a MLG flake. The three corners are presented by red arcs, θ and r are the angle in radians, and radius of the bottom corner, respectively, while d is the interlayer distance. (e) The lattice spacing at the selected areas marked by yellow and red boxes in (d), the interlayer distance increased from 0.33 nm at the flat region, to 0.41 nm at the strained region. (A colour version of this figure can be viewed online.)

configuration of the wrinkle should meet the following requirements: First, in the top layer (l = 1, see Fig. 5c), the length of the two bottom arcs (as well as the length of the top arc in the first layer) should be a multiple of the carbon-carbon (C-C) bond length L_{c-c} ($\theta r = nL_{c-c}$ where n = 1, 2, 3). Secondly, the arc length difference between neighboring layers needs to be an integer times the C–C bond length. for example in the first laver and second laver. $\theta(r+d)-\theta r=n'L_{c-c}$ (n'=1,2,3...). Thirdly, the sum of the three-arc lengths in each layer should be the same. Under these three conditions, the curved regions at the wrinkles are no longer in an ABstacked arrangement; this stacking disorder and perhaps more importantly, the significant increase in interlayer separation (see comments above on HRTEM data), leads to a weakening of interlayer coupling. Since the band structure of layered materials is closely related to interlayer coupling, this new method for fabricating wrinkle structures could be useful to tailor the band structure of layered materials to bring about unprecedented electronic, optical and mechanical properties.

3. Conclusion

Wrinkle networks were generated in multilayer graphene (MLG) flakes that were exfoliated from graphite onto a PDMS substrate; the assembly was repeatedly dipped into and taken out of liquid nitrogen and the rapid cooling of the PDMS caused it to contract resulting in compressive stress leading to the formation of wrinkles in the MLG flakes. This method also generated wrinkle networks in multilayer MoS₂, WSe₂, and GaS flakes and should thus work with any sufficiently thin platelet with appropriate aspect ratio (lateral dimension divided by thickness). Both atomic resolution AFM and hydrogen plasma etching coupled with microscopy show that wrinkles in MLG flakes are generated along the armchair direction. Raman spectra and Raman mapping show that the 2D band is sensitive to wrinkles; the intensity of the 2D⁻ peak is increased while that of the 2D⁺ peak is decreased on top of a wrinkle compared to the flat regions. Raman results show that the interlayer coupling of multilayer graphene is weaker in the strained region but not in the AB-stacked flat regions primarily due to the deformation leading to a larger interlayer separation, and also to the misalignment of the graphene layers away from perfect AB stacking.

4. Experimental section

Sample preparation and AFM characterization: PDMS films were used as substrates to cleave relatively thick multilayer graphene (MLG) flakes through a process similar to mechanical exfoliation of graphene [49]. Each of the PDMS/MLG flake samples was immersed in liquid nitrogen contained in a small Dewar for a given time. In order to increase the cooling rate, the samples were shaken slightly when immersed in the liquid nitrogen. The sample was taken out of the Dewar after bubbling from the PDMS stopped (usually 5 s), from which, we roughly estimated the cooling rate to be around 40 °C/s. Wrinkles were generated on the MLG flakes during the cooling process. The MLG flakes with wrinkles were transferred onto other substrates such as silicon wafer pieces having a 300 nm-thick thermal oxide layer by standard transfer techniques using PMMA films. Optical microscope (6XB-PC, Shang Guang) was used to capture the images of wrinkles. Wrinkles on exfoliated flakes of the three other layered materials were prepared by the same method. AFM characterization of wrinkles was done with Bruker Dimension Edge, and Asylum Research Cypher (AR Cypher), atomic force microscopes (AFM) in tapping and contacting modes, respectively. The AR Cypher AFM was used to obtain atomic resolution images. Since monolayer and few layer graphene (<10) always follow the morphology of the substrate, they would not be expected to form regular wrinkle structures and "straight and regular" wrinkles running along only the armchair direction could only be observed on MLG flakes.

Hydrogen plasma etching experiments: Hydrogen plasma etching was done in a custom-made remote plasma system. Inductively coupled plasma was generated at one end of a 6.5 cm diameter quartz tube furnace using a radio frequency (RF) coil. The MLG flake samples with wrinkles transferred on Si wafer with 300 nm-thick thermal oxide layer were heated by placing them at the center of a furnace (400 °C), which was separated from the RF coil by a distance of about 20 cm. The plasma was generated outside the furnace and carried downstream to reach the sample. The pressure in the tube furnace was fixed at about 0.1 Torr with hydrogen flowing at 30 sccm under vacuum pumping.

Raman measurements: Confocal Raman spectroscopy/microscopy (WITec Alpha 300) was used to measure spectra and geometry of the wrinkles formed in the MLG flakes. A laser wavelength of 532 nm and spot size of ~0.5 μ m were used to obtain the Raman spectra and mapping images.

TEM measurements: The wrinkle sample for TEM measurement was prepared by Focused Ion Beam Microscopy (FIB, FEI DB235). The structure of the multilayer graphene wrinkle was studied by high-resolution transmission electron microscopy (HR-TEM, FEI Titan3 G2 60–300).

Conflicts of interest

The authors declare no conflict of interest.

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Appendix A. Supplementary data

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