ACS APPLIED NANO MATERIALS

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Biomimetic Combs as Antiadhesive Tools to Manipulate Nanofibers

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Cite This: *ACS Appl. Nano Mater.* 2020, 3, 3395−3401

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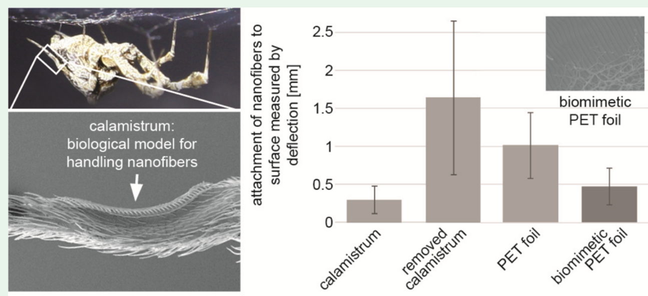
ABSTRACT: Nanofibrous multifunctional materials have attracted a lot of attention because of the benefits of their special structure. Despite the diverse benefits of nanofibrous materials, their inherent stickiness to any surface is a major obstacle in producing and processing such materials. There are many paragons in which biological models or elements from nature have been biomimetically adapted in various areas in order to resolve technical problems, such as the silent flight of the owl, the lotus effect, or the sticky feet of the gecko. One special example shows us how nanofibers might be handled in the future: cribellate spiders possess a specialized comb, the calamistrum, on their hindmost legs, which is used to process and assemble nanofibers into structurally complex capture threads. Within this study, we were able to prove that these fibers do not stick to the calamistrum because of a special fingerprint-like nanostructure on the comb. This structure prevents the nanofibers from smoothly adapting to the surface of the comb, thus minimizing contact and reducing the adhesive van der Waals forces between the nanofibers and surface. This leads to the spiders' ability of nonsticky processing of nanofibers for their capture threads. The successful transfer of these structures to a technical surface proved that this biological model can be adapted to optimize future tools in technical areas in which antiadhesive handling of nanofibrous materials is required.



KEYWORDS: *functional morphology, spider, cribellate, van der Waals, bionic, laser-induced periodic surface structures*

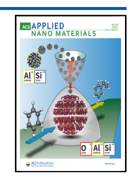
■ INTRODUCTION

Nanomaterials and nanofibers are constantly drawing the attention of material scientists and engineers because their surface-to-used-material ratio is favorable for medical applications, filter technology, or smart textiles.[1−4] Because of their inherently small scale, production and further processing of these materials are difficult. For example, processing nanofibers is challenging because they are likely to adhere to any surface because of van der Waals forces. Despite attempts to facilitate the controllable production of nanofibers,[3−7] diverse applications based on nanofibers are still limited because the handling of nanofibers remains the main problem.

In nature, there are animals that are actually able to produce, process, and handle nanofibers: cribellate spiders (Figure 1a).[8,9] They use these nanofibers as an adhesive wool to capture prey, embedding the fibers into the viscous waxy layer of the insects' cuticle.[10] For one thread, between 5000 and 30000 single fibers of 10−30 nm thickness are extracted from the cribellum (spinning plate anterior to the other spinnerets) without using any electric charge (Figure 1d).[11,12] To support the extracted sheet of nanofibers, differently sized fibers, such as axial fibers (Figure 1d,e), are assembled by the movement of the spinnerets, thus forming one complex-structured capture thread.[8,9]

Spiders cannot eject their silk from the spinnerets but have to extract it, e.g., by grabbing the silk with their feet. Hence, it was assumed that the nanofibers are extracted by the calamistrum, a comblike structure of modified setae on the metatarsus of the hindmost (fourth) legs, and it was assumed that fiber extraction is the only function of the calamistrum (Figures 1b,c and 2a,b). However, recent studies proved that the calamistrum is not necessary for the extraction of nanofibers. It rather induces the formation of the typical puffy outer structure of the nanofibers in the thread.[8,11] This suggests that the calamistrum also processes the nanofibers instead of simply extracting them, possibly by influencing the protein conformation.[12] In general, not much is known about the functionality of this specialized comb. Nevertheless, it could give us an indication of how we could handle nanofibers more easily in the future. The correct contact between the calamistrum and nanofibers seems to be crucial for nanofiber handling because all cribellate spiders studied so far show behavioral adaptations during web construction in order to maintain it.[9]

Received: January 15, 2020
Accepted: March 16, 2020
Published: March 16, 2020



https://dx.doi.org/10.1021/acsanm.0c00130
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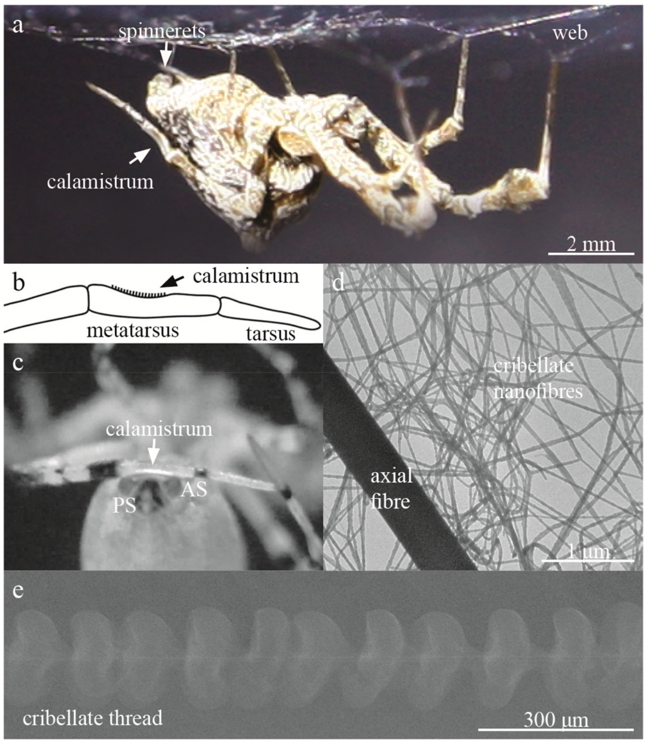

Figure 1. (a) *U. plumipes* in its resting position. On the hindmost (fourth) leg, the calamistrum on the metatarsus can be seen. (b) Schematic drawing of the fourth leg of the cribellate spider with the calamistrum position on the metatarsus. (c) Uloborid *Zosis geniculata* brushing its calamistrum over the spinnerets (AS, anterior spinneret; PS, posterior spinneret) during capture thread production. (d) TEM image of a cribellate thread, showing the axial fibers and the bundle of cribellate nanofibers. (e) Overview of the cribellate capture thread, without any coating, in the SEM.

This study aims to shed light on the special antiadhesive property of the calamistrum, which renders this tool suitable for nanofiber handling. Furthermore, the potential for biomimetic transfer is analyzed. We therefore studied the calamistrum of the orb-weaving uloborid *Uloborus plumipes* (feather-legged lace weaver; Figure 1a) and transferred the found principle to a biomimetic foil, thus creating a nonsticking surface for nanofibers.

RESULTS

Antiadhesive Properties of the Calamistrum. A previous study of *U. plumipes* showed that removal of the calamistra has an influence on the structure of the nanofibers in the capture threads rather than inhibiting their extraction.[8] Upon observation of modified spiders, the typical combing movement was still performed during capture thread production. However, in all cases where the calamistrum was removed, residues of fibers clotted the original location of the calamistrum (Figure 2c). Such a clotting was never observed on unmodified spider legs. Hence, the calamistrum functions as an antiadhesive surface and prevents the spider from adhering to its own nanofibers during their extraction. These results were confirmed by comparing the antiadhesive properties of legs with native calamistra to those with shaved-off calamistra. The nanofibers adhered significantly better to the legs without a calamistrum ($p < 0.001$; Figure 2d). It can therefore be assumed that a special feature of the calamistrum is to provide antiadhesive properties toward nanofibers, e.g., by a reduction of van der Waals forces. Such a reduction of adhesive forces due to van der Waals energies could be achieved either by a reduction of the contact area, by an increase of the distance of the interacting surfaces, or

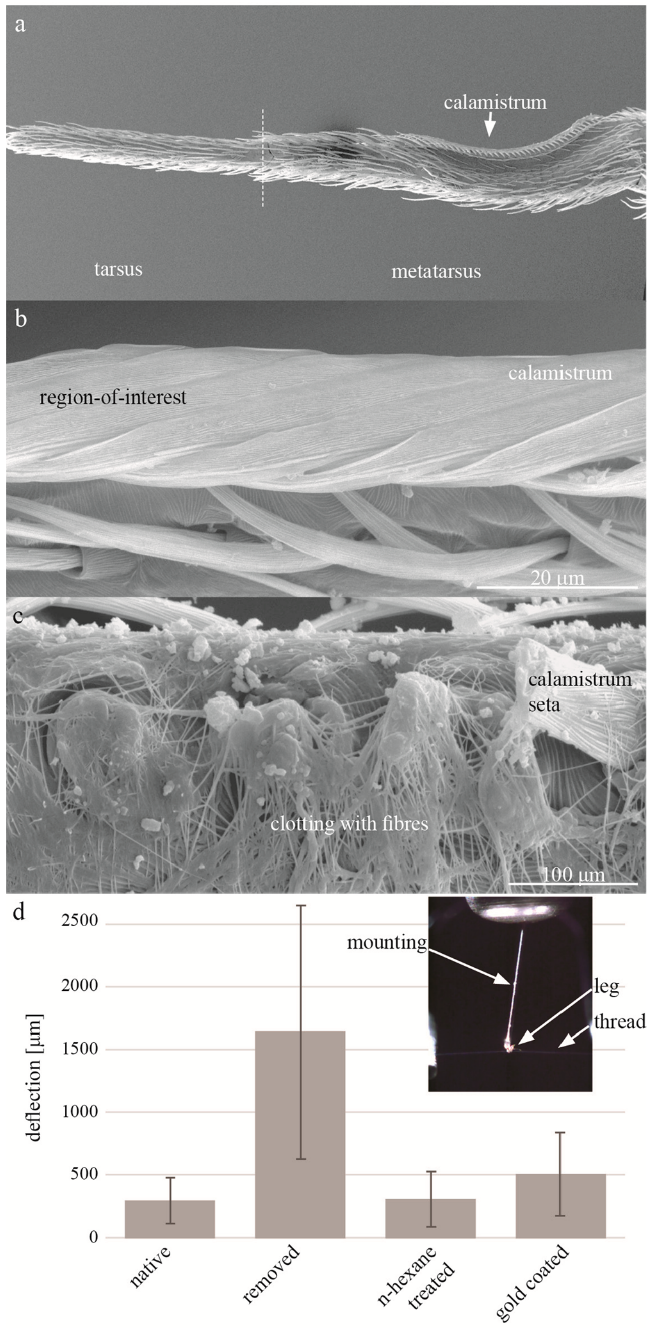

Figure 2. (a) SEM of the metatarsus and tarsus of the fourth leg, showing the depression where the calamistrum is situated as a specialized row of setae. (b) SEM close-up of the calamistrum. (c) Fibers clotting the metatarsus of spiders with removed calamistra. Please note the stub of the calamistrum set on the right side, having fewer nanofibers. (d) Indirect measurement of the adhesive forces between the calamistrum (native, removed by shaving, or surface chemistry changed by either washing with *n*-hexane or coating with gold) by measuring the deflection of a 7-mm-long cribellate thread. Inset: Maximal deflection of the cribellate thread attached to the calamistrum.

https://dx.doi.org/10.1021/acsanm.0c00130
ACS Appl. Nano Mater. 2020, 3, 3395−3401

generally by making the interacting state (close contact of the surfaces) energetically less favorable than a separated geometry.

Antiadhesive properties could be accomplished through either specialized surface coating or surface structuring. Measuring the adhesive forces of native calamistra and those of calamistra without cuticular hydrocarbons (i.e., wax coating of the spider, removed by *n*-hexane), toward the cribellate nanofibers, proved no significant difference ($p = 0.83$; Figure 2d). However, gold coating led to a slightly better adhesion of the fibers toward the calamistrum ($p = 0.04$). Because coating our samples with gold also leads to a slight change of the surface structure (thickness of gold layer ∼10 nm), we, nevertheless, assume that a structural component has to cause the antiadhesive properties. To understand why the calamistrum of *U. plumipes* is nonsticky to nanofibers, we observed the morphology of the calamistrum more closely. Upon close observation with scanning electron microscopy (SEM), one can see that its surface is covered with fingerprint-like nanoripples running parallel to the length of the single calamistrum seta (Figures 2b and 3a). During the combing process, the nanofibers are pulled orthogonally over these ripples.

Theoretical Modeling of Interaction. The detailed characterization of the contact area in previous studies enabled us to calculate van der Waals forces between the nanofibers and region of interest (i.e., contact area; Figures 2b and 3b) on the calamistrum in *U. plumipes*:[9,13]

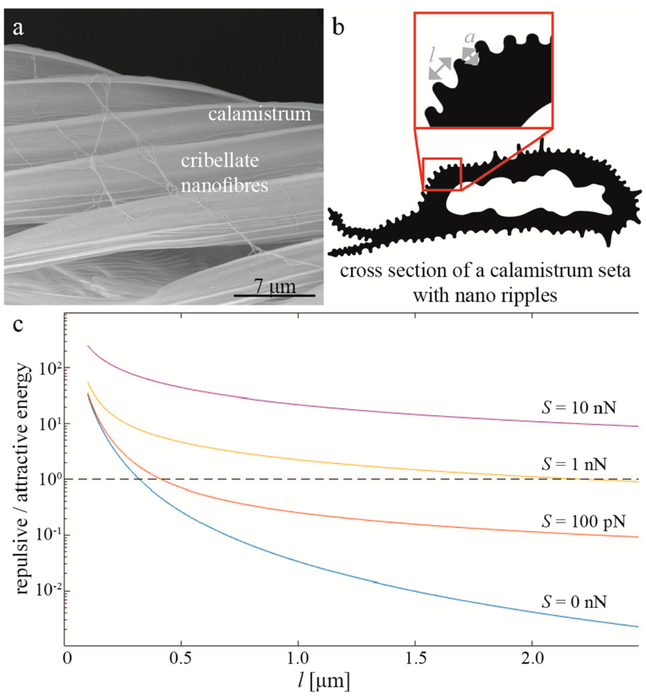

Figure 3. (a) SEM close-up of single cribellate nanofibers placed artificially over the calamistrum. Note the surface structure on the calamistrum. (b) Schematic cross section through one calamistrum seta at the region of interest. Please note that the setae are overlapping each other, and thus not all of the calamistrum surface typically comes into contact with the nanofibers. More images of the calamistrum setae can be found in Figure S1. (c) Theoretical model of the repulsive versus attractive energy depending on the distance *l* between the nanostructures as well as the longitudinal force *S* on the fibers (as the fibers are being pulled over the calamistrum in the natural model).

The cross section of the calamistrum's surface in contact with the nanofibers can be approximated as a cosine function. In order to have full contact with the surface, any fiber along this cross section has to deform according to

$$w(x) = a\cos\left(\frac{2\pi x}{l}\right) \tag{1}$$

with a being the amplitude of the cosine function (i.e., height of the nanostructure) and l being the wavelength (i.e., peak-to-peak distance). With eq 1 as a function for the deflection, we obtain the derivations (inclination and curvature)

$$w' = \frac{dw}{dx} = \frac{-2\pi a}{l}\sin\left(\frac{2\pi x}{l}\right)$$
$$w'' = \frac{d^2w}{dx^2} = \frac{-4\pi^2 a}{l^2}\cos\left(\frac{2\pi x}{l}\right) \tag{2}$$

In the deflected fiber, the stored potential energy can be estimated according to linear elastic (Hookean) beam theory (Euler–Bernoulli beam theory)

$$U_B \approx \frac{EJ}{2}\int_0^l w''^2\, dx \tag{3}$$

with E being the Young's modulus and J denoting the second moment of the area (moment of inertia of the plane area). If the fiber is now stressed by a longitudinal force S (i.e., being pulled over the calamistrum during extraction), then according to the theory of strings, the potential energy of the deformed fiber can be estimated by

$$U_S \approx \frac{S}{2}\int_0^l w'^2\, dx \tag{4}$$

Thus, a fiber under stress (U_S) and deformed for fitting the surface contour (U_B) stores the potential energy that can be obtained by inserting eq 2 into eqs 3 and 4. After integration, we obtain the energy (work, U) necessary to deform the fiber according to the surface profile by summing up U_B and U_S.

$$U \approx a^2\pi^4\left(\frac{4EJ}{l^3} + \frac{S}{l}\right) \tag{5}$$

When deformed, however, the energy due to van der Waals interactions is reduced. The interaction energy per unit length of a cylinder (i.e., nanofiber) of radius R with a parallel cylinder of radius R_1, separated by a distance d, can be calculated[14] as

$$G = -\sqrt{\frac{2R_1R}{R_1 + R}}\,\frac{A_H}{24d^{3/2}} \tag{6}$$

with the Hamaker constant A_H. In order to calculate the interaction forces between our fiber and a semiinfinite body (because the calamistrum is much larger than the fiber), we need the radius R_1 to go to infinity. Thus, we obtain

$$\mu = \lim_{R_1\to\infty}(G) = -\sqrt{2R}\,\frac{A_H}{24d^{3/2}} \tag{7}$$

The van der Waals energy obtained due to the interaction is

$$U_{vdW} = \mu l_{tot} \tag{8}$$

The total interaction length l_{tot} of the fiber with a cosinusoidal surface can be calculated for one period (wavelength l) as

https://dx.doi.org/10.1021/acsanm.0c00130
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$$l_{tot} = \int_0^l \sqrt{1 + w'^2}\ dx \tag{9}$$

For our cosine function, this integral can be solved as

$$l_{tot} = \frac{2l}{\pi} E\left(2\pi j \frac{a}{l}\right) \tag{10}$$

with $E(x)$ being the total elliptical integral of the second kind of x. However, this rather complex function can be approximated as

$$l_{tot} \approx \max(l,\ 4a) \tag{11}$$

Thus, we obtain

$$U_{vdW} \approx -\sqrt{2R}\frac{A_H}{24d^{3/2}}\max(l,\ 4a) \tag{12}$$

While the potential energy U increases the total energy in the system (i.e., it renders the deflected state unfavorable), the van der Waals energy U_{vdW} due to the negative sign lowers the energy, and this makes the deflected state favorable. So, U_{vdW} leads to attraction, while U leads to repulsion. If the absolute value of U is larger than the absolute value of U_{vdW}, we expect the interaction to be weak and adhesion of the nanofibers to the calamistrum unlikely. Whereas if the absolute value of U is smaller than the absolute value of U_{vdW}, adhesion is energetically favorable. Therefore, to quantify whether the surface is adhesive or antiadhesive, we calculate the ratio

$$\Gamma = \frac{U}{-U_{vdW}} = \frac{a^2\pi^4\left(\frac{4EJ}{l^3} + \frac{S}{l}\right)}{\sqrt{2R}\frac{A_H}{24d^{3/2}}\max(l,\ 4a)} = \frac{12a^2\pi^4(Sl^3 + 4EJ)\sqrt{2d^3}\max(l,\ 4a)}{l^3\sqrt{R}A_H} \tag{13}$$

Thus, $\Gamma > 1$ means antiadhesion, and $\Gamma < 1$ corresponds to adhesion of the nanofibers to the surface. For a fiber thickness of $R = 20$ nm, a depth of the nanostructure of 200 nm ($a = 100$ nm; Figure 3b), a varying distance l between the nanostructures, $J = \pi R^4/4$, $A_H = 45 \times 10^{-21}$ J,[15,16] a distance $d = 0.165$ nm (i.e., van der Waals forces become relevant[15,16]), and a Young's modulus of $E = 80$ MPa,[17] this ratio is calculated for various loads S (Figure 3c). Our calculations prove that, as soon as there is as little as a 1 nN load on the fiber, the distance between the nanostructures starts to not matter and the repulsive energy is always higher. However, on the calamistrum of *U. plumipes*, the distance between the nanostructures is 200−300 nm. So, even without any load, the repulsive energy should always be higher than the attraction.

Biomimetic Antiadhesive Foil. To prove our theory and substantiate our calculation, artificial poly(ethylene terephthalate) (PET) foils with nanostructures similar to that of the calamistrum were produced by laser processing (Figure 4a; distance $l \approx 350$ nm and depth of the nanostructure ≈ 100 nm). As expected, comparing foils with and without structure, the biomimetically structured foil always proved less adhesion toward the nanofibers ($p = 0.04$ (uncoated foils) and $p < 0.0001$ (gold coated foils); Figure 4b). Gold coating was performed to reduce electrostatic interaction, which was observed in uncoated PET foils (i.e., deflection of thread even before contact). The structured gold-coated foil was not significantly different in its antiadhesive properties compared to the gold-coated calamistrum ($p = 0.72$) and only slightly worse than the native calamistrum ($p = 0.02$). Thus, we presume that the fingerprint-like nanopatterns on the calamistrum are responsible for its antiadhesive properties. These patterns can be mimicked on biomimetic foils, showing the same antiadhesive properties toward nanofibers as the biological model.

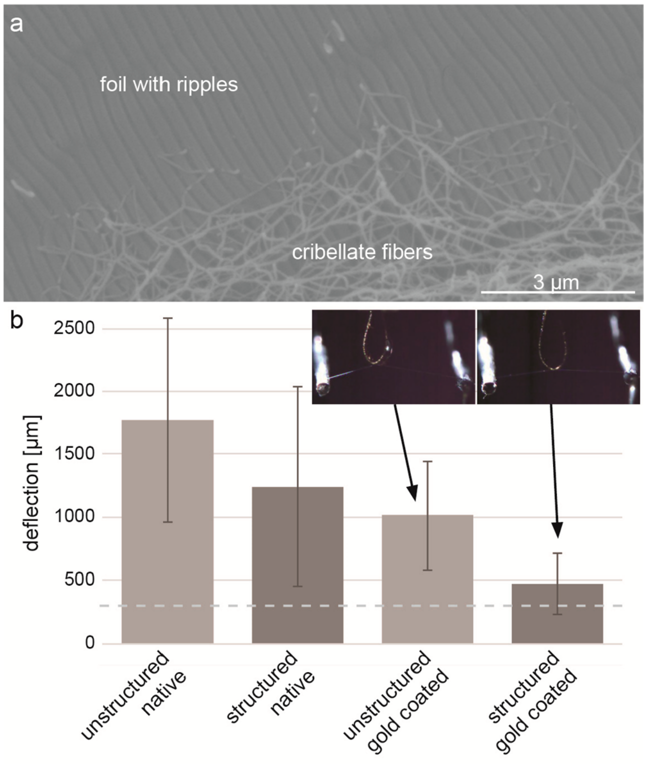

Figure 4. (a) Foil with nanoripples as a biomimetic replication of the calamistrum, with artificially placed nanofibers on its surface. (b) Indirect measurement of the adhesive forces between the biomimetic foil (unstructured vs structured, as well as not gold-coated vs gold-coated) by measuring the deflection of a 7-mm-long cribellate thread (insets: maximal deflection of the cribellate thread attached to a gold-coated structured and to an unstructured foil). The dashed line indicates the mean value of the data measured for the native calamistrum.

■ DISCUSSION

Since the discovery of the spatula of geckos' feet enabling it to stick to the wall through van der Waals forces, these forces are assumed to play a major role in any nanofibrous system.[15,16,18,19] In fact, technical nanofiber processing, transportation, or simple things such as spooling are inhibited by their attraction to any surface.[20] Cribellate spiders, though, produce, process, and handle nanofibers during their capture thread production that are much smaller than most technical nanofibers[21,22] and therefore should adhere well to any surface. These spiders have a specialized comb, the calamistrum, which shows antiadhesive properties toward the nanofibers. Investigating the function of this comb, we were able to prove that, because of a special fingerprint-like nanostructure on its contact area, repellent forces dominate over adhesive van der Waals forces. This nanostructure can be used as biomimetic inspiration to enable the processing of nanofibers in the future.

https://dx.doi.org/10.1021/acsanm.0c00130
ACS Appl. Nano Mater. 2020, 3, 3395−3401

Our successful creation of a biomimetic antiadhesive foil stresses the application potential of our result.

Implications for the Biological Model. In biological research, several studies highlighted how spiders avoid sticking to their own glue. Some spiders have a coating, protecting them from their capture threads.[23,24] However, these spiders have gluey capture threads, whereas cribellate spiders produce nanofibers to capture prey. Although their adhesive mechanism depends on the surface chemistry of the prey, nanofibers like cribellate fibers stick to any surface via van der Waals forces.[10,15] The calamistrum's exact functionality was ill-defined, after it had been proven to be unnecessary for fiber extraction.[8,11] We demonstrate in this study that a particular surface nanotopograhy on the calamistrum is used by the spider to prevent sticking to its own nanofibers during processing. In conclusion, this antiadhesion is not due to a coating, as described for spiders with gluey capture threads, but due to a nanostructure preventing adaptation of the nanofibers to the surface and thus decreasing van der Waals forces.

Antiadhesive Surface by a Nanostructured Surface. The reduction of van der Waals forces by reducing the contact area through a specialized nanostructure is a new path for producing antiadhesive surfaces, enabling easier nanofiber handling in the future. Other forces, though, can also have an impact on fiber adhesion on surfaces. For example, the influence of electrostatic forces is still discussed as an adhesive mechanism of the setae of the gecko.[25] Also, in our experiments, the foils where easily electrostatically charged if not coated with gold, visible by an attraction of the thread toward the foil. However, because an induced conductivity of the tool renders the effect irrelevant, the here-observed effect should not have any major implication for technical applications. For example, electrospun technical nanofibers are charged during their manufacturing process but typically collected on a conductive target.[26] In addition, humidity has a significant influence on the air conductivity, leading to changes in the electric field in which the electrospun fibers are drawn. Hence, modern electrospinning setups are often built in a climate chamber.

Nevertheless, in the calamistrum as well as for the technical replication, some remaining adhesive forces were still there, leading to very low adhesion of the nanofibers toward the structured surfaces. Further experimental setups could examine these minor adhesive forces to see if they are low enough to not interfere with nanofiber processing. On the other hand, reduced adhesion forces might facilitate an easier cleaning of the tools even if residual fibers would stick to the surfaces. In either of these cases, such an antiadhesive surface would be very interesting for technical applications because no such surface property has been described yet. Hence, the feather-legged lace weaver, *U. plumipes*, provides biomimetic inspiration for nanostructured foils, enabling easier handling and processing of nanofibers in the future.

CONCLUSION

Inspired by the biological model of the cribellate spiders, a novel surface with antiadhesive properties of nanofibers, due to reduced van der Waals forces, can enable the processing of nanofibers. The calamistrum, a special comb found in cribellate spiders that is used to process the spider's nanofibers has a fingerprint-like nanostructure, reducing the stickiness of the calamistrum. This feature can be mimicked by laser-induced periodic surface structures (LIPSSs) on PET foils, rendering these foils also antiadhesive. In practical applications, such structured surfaces could be used, for example, as collectors in electrospinning setups, making it easier to strip off the nonwoven nanofiber fabric.

MATERIAL AND METHODS

Ethics. The species used in the experiments is not an endangered or protected species. Special permits were not required. All applicable international, national, and institutional guidelines for the care and use of animals were followed.

Study Animals. *U. plumipes* (Lucas, 1846) were raised separately under room temperature, humidity, and northern European diurnal rhythm. Once a week, the spiders were fed with fruit flies. Water was provided once to twice per month by sprinkling the enclosure. Such wetted webs were not used for further research. To visualize nocturnal movements of the spiders, video recordings were made using a webcam (Logitech HD Webcam C270, Apples, Austria; software, Logitech Webcam Software Version 2.5.1) and a red light source (gooseneck lamp with a red light filter). Because of low resolution, it was only possible to determine whether spiders were performing the combing movement at all or not.

The calamistra were removed after the protocol of Joel et al.[8] The fourth legs of these spiders were air-dried and used to analyze the prior location of the calamistrum. Because spiders possess an exoskeleton, air-drying does not change the outer structure of the leg. For this, the samples were sputter-coated with a ∼10 nm layer of gold (Hummer Technics Inc.) before examination with a scanning electron microscope (SEM 525 M, Philips AG, Amsterdam, The Netherlands).

To study the antiadhesion of the calamistrum toward nanofibers, spiders were killed by freezing at −20 °C, and the fourth legs were removed from the body and glued to a thin metal wire with superglue, always checking for correct positioning of the calamistrum using a microscope. Before fixation to the metal wire, the calamistra were either removed, used native, or washed twice with *n*-hexane or coated with gold, the latter two to change the surface chemistry.

Production of Structured Foil. For the formation of LIPSSs, PET foils were irradiated by the linearly polarized light of a pulsed KrF excimer laser (laser wavelength λ = 248 nm; pulse length τ = 20 ns). The linear polarization was obtained by means of a Glan-Thomson polarizer, which was passed only by the central rather homogeneous part of the laser beam. The laser beam was attenuated by a dielectric polarizer and projected onto the inclined sample by cylindrical fused-silica lenses. The periodicity and height of the LIPSS structures depend on the laser wavelength λ, the angle of irradiation θ, the number of pulses N, and the laser fluence ϕ.[27] We used λ = 248 nm, θ = 30°, N = 6000 pulses (at a repetition rate of 10 Hz), and $\phi \approx$ 10 mJ/cm^2. The resulting LIPSS structure had a periodicity of $\Lambda \approx$ 350 nm and a structural height of $h \approx$ 100 nm. The samples were cut into 5-mm-long stripes and bent before fixation in a sample holder to make them edgeless and avoid entanglement. The foils were tested with and without structuring, as well as with and without gold coating. Gold coating was used to avoid any influence of the changed surface chemistry and/or changed electrostatic surface charges due to laser irradiation.

Antiadhesion Experiments. Pieces of capture threads (7 mm) were spun between two metal wires and placed in the focus of a high-speed video-recording microscope (VW-9000C; Keyence Corporation, Osaka, Japan). Using a micromanipulator (MM 33; Märzhäuser Wetzlar GmbH & Co. KG, Wetzlar, Germany), the samples (calamistra and foils) were brought into contact with the thread. A thread deformation via a downward motion of the micromanipulator of 1−2 mm confirmed contact, whereupon the sample was slowly and constantly drawn away from the thread until detachment. At a magnification of 10−20× and a speed of 125 fps, videos of the deformation of the thread as well as the final detachment were recorded. To reduce the influence of electrostatics, samples and holders were shortly grounded before each experiment and, if necessary, the air was ionized with the help of a Milty Zerostat 3

https://dx.doi.org/10.1021/acsanm.0c00130
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(Armour Home Electronics Ltd., Bishop's Stortford, U.K.). This is an antistatic device preventing the formation of static charges. Additionally, the experiments were shuffled and carried out over several days. All experiments in which a high deformation of the thread was still visible even before the sample touched the thread were discarded.

The calamistra experiments were repeated 15 times and the foil experiments 20 times. Videos were analyzed using a Keyence VW-9000 motion analyzer (version 1.4.0.0), measuring the strongest deflection of the thread before detachment of the surface. Please note that in two cases the detachment did not occur in our field of vision, so we took the maximal value measured in the data set twice. Raw data are presented in the supplement.

A normal distribution of data was tested with a Kolmogorov–Smirnov test (GNU PSPP Statistical Analysis Software, version 1.2.0-g0fb4db). After verification of the normal distribution, a *t* test (Excel, 2016) was performed, comparing single data sets.

Morphological Parameters for Theoretical Modeling. Using the data of focused-ion-beam (FIB)-SEM tomography (Heiss et al.[13]) as well as FIB milling (FEI Strata 200; Figure S1; sample preparation as described for FIB-SEM tomography), we measured the depth and peak-to-peak amplitude of the nanostructures covering the calamistrum at the region of interest (close to the tips of the calamistrum setae; refer to work by Joel et al.[9]). We additionally used SEM images of the calamistrum to measure the peak-to-peak distance. To measure the nanofiber diameter, thread samples were transferred to finder grids (Plano GmbH) and observed without any further treatment via transmission electron microscopy (TEM; model TEM 10, Carl Zeiss). Data used from other sources are quoted accordingly.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.0c00130.

- Raw data of the antiadhesion experiments and images of FIB-milled calamistra (PDF)
- Exemplary trial of antiadhesion testing of the native calamistrum toward the cribellate capture thread (AVI)
- Exemplary trial of antiadhesion testing of an unstructured native foil toward the cribellate capture thread (AVI)
- Exemplary trial of antiadhesion testing of a structured gold-coated foil toward the cribellate capture thread (AVI)

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Author Contributions

H.A. and A.-C.J. removed calamistra of the spiders. The biomimetic foil was produced by J.H.. M.M. performed antiadhesion experiments. D.P. performed FIB milling. A.H. performed FIB-SEM tomography. A.H. and D.P. created a 3D model of the calamistrum from the FIB-SEM tomography data. EM sample preparation as well as examination was done by A.-C.J. and M.M. W.B. performed the calculations. A.-C.J. designed the study, analyzed data, and wrote the first draft of the manuscript. All authors contributed to the writing of the manuscript and have given approval to the final version of the manuscript.

Funding

This work was supported by the European Union's Horizon 2020 research and innovation program within the project "BioComb4Nanofibers" (Grant 862016), the Excellence Initiative of the German federal and state governments, and the German National Science Foundation (JO 1464/1-1 and JO 1464/2-1 to A.-C.J.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank C. F. F. Grannemann, M. Haaße, and F. Hischen for preliminary antiadhesion testing. We also thank Paul Sloan (M.A.) for language editing in this manuscript.

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