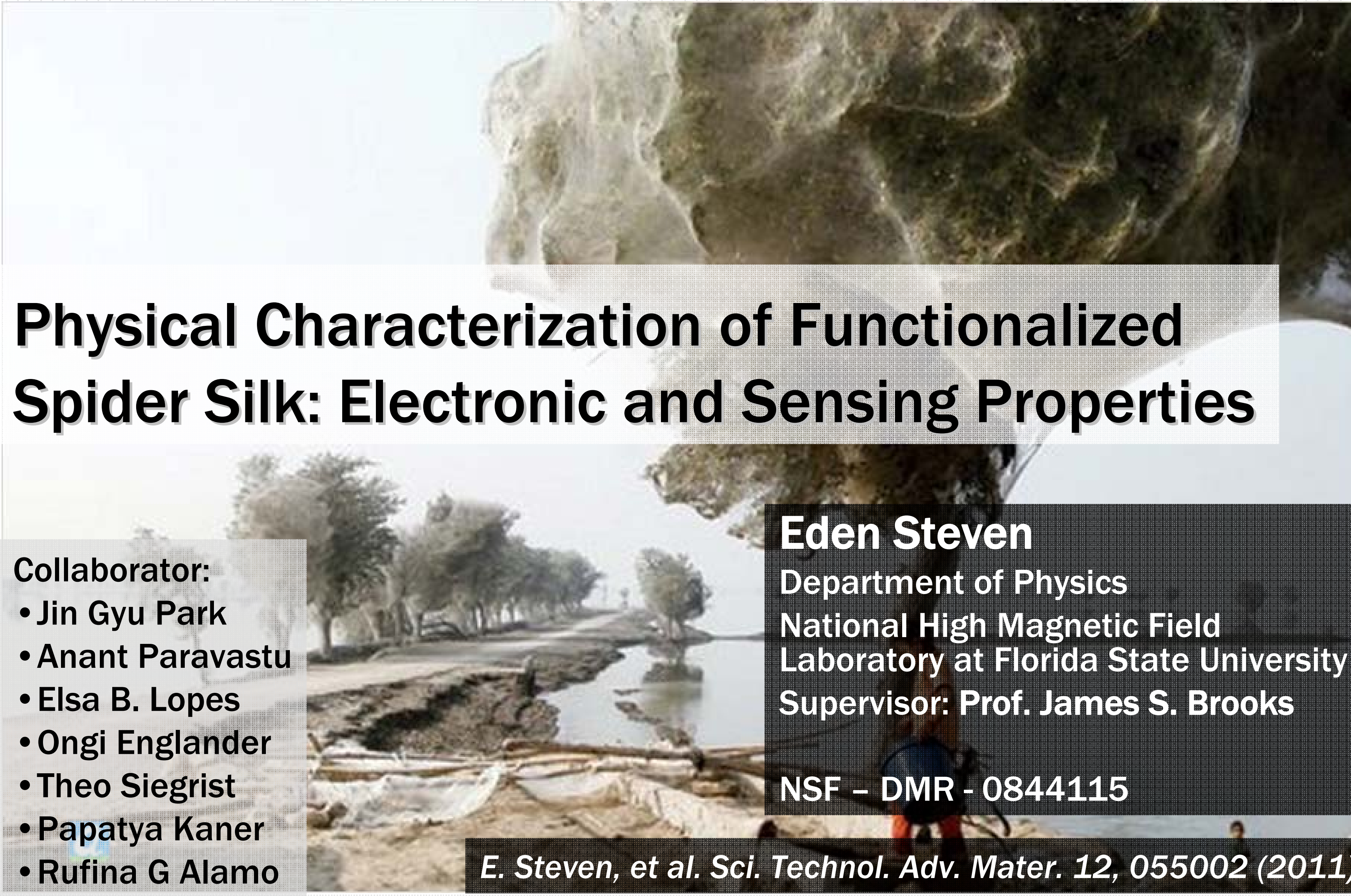

Physical Characterization of Functionalized Spider Silk: Electronic and Sensing Properties

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NSF – DMR - 0844115

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- Theo Siegrist
- Papatya Kaner
- Rufina G Alamo

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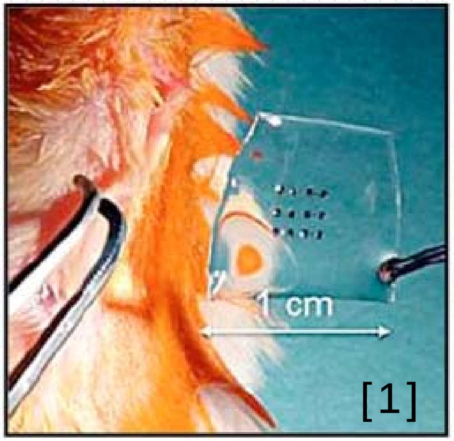
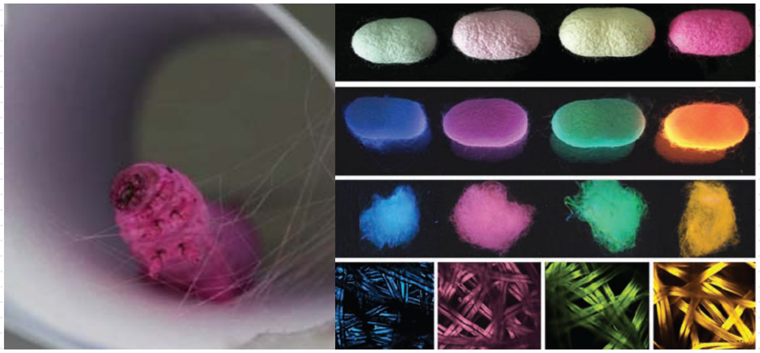
Trends in spider silk research

- As substrate for implantable devices



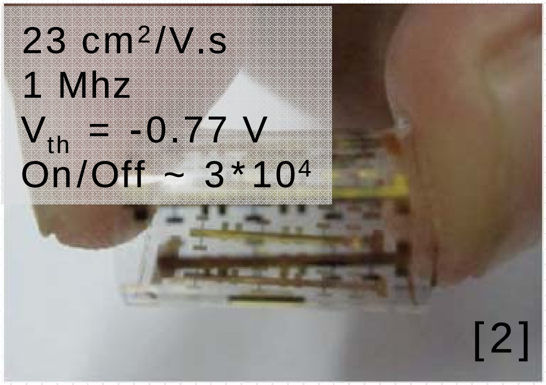
- Dyed-silkworm for intrinsically colored silk. Added functionality: anticoagulant, anti-inflammatory



[3]

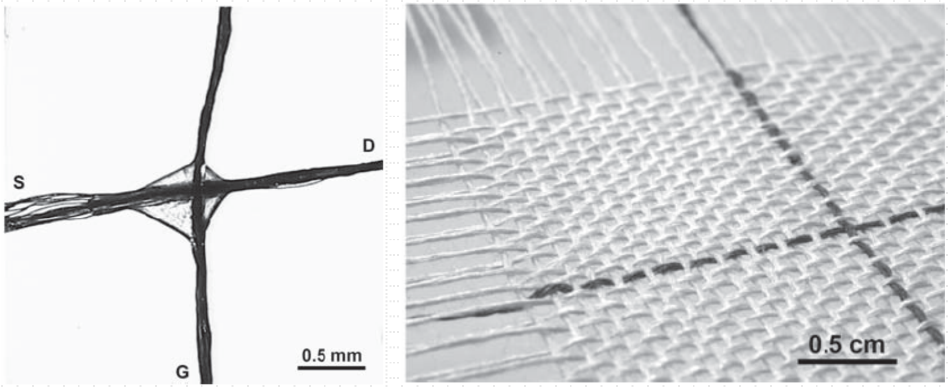
- Modified goat for mass-production of spider silk. Bulletproof skin.

- As gate dielectric for flexible OTFT (pentacene)



- Novel approach to electronic circuits. Woven electrochemical transistors on silk fibers

[4]



[1] D.H. Kim, et al. APL **95**, 133701 (2009)
[2] C.H. Wang, et al. Adv. Mater. **23**, 1630 (2011)
[3] N.C. Tansil, et al. Adv. Mater. **23**, 1463 (2011)
[4] C. Muller, et al. Adv. Mater. **23**, 898 (2011)

Motivation and outline

- Lack of electronic characterization of spider silk in literature.
- Application in unconventional areas.

Protein structures

↓

Neat spider silk – Humidity dependent conductivity

↓

I_2-doped silk
- Effect on conductivity & pyrolization
- MAS-NMR and FTIR of I_2-doped silk, Qualitative model

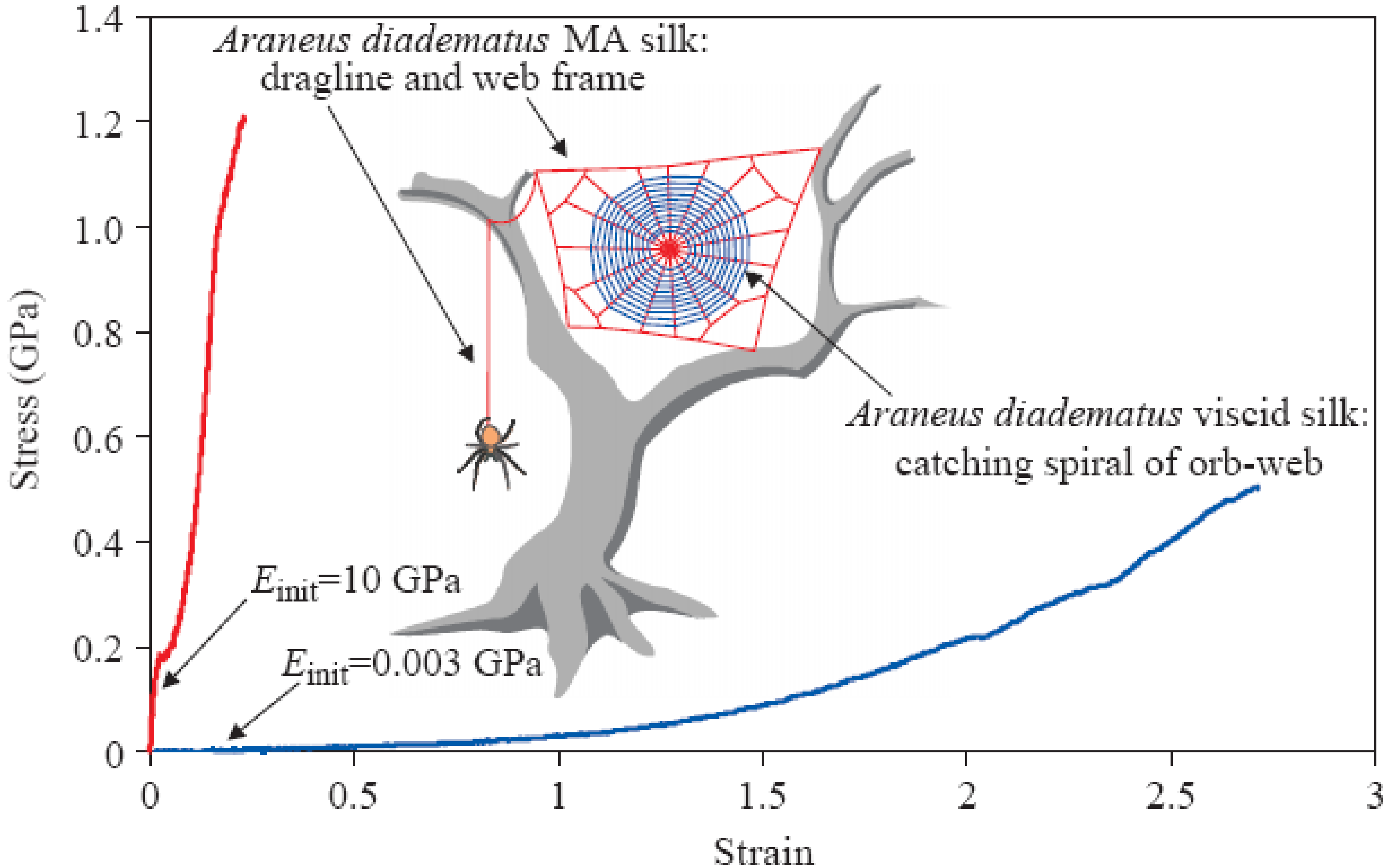
↓

Gold sputtered silk
- Good adherence to silk
- MAS-NMR of Au-sputtered silk
- Application: Electrical junction, flexible and clean electrodes

↓

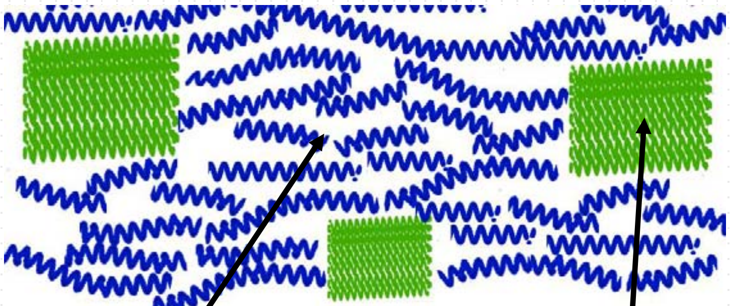
Future work – CNT-coated/doped spider silk as pulse sensor

Mechanical properties



J.M. Gosline. J. Exp.Biol, 202, 3295 (1999)

Protein structure



3_1 Helix
Flexible segment
Glycine-rich

β-sheet
Harder segment
Alanine-rich

Spidroin 1

GQG GYG GLG SQG A GRG GLG GQG A GA_7G_2 A

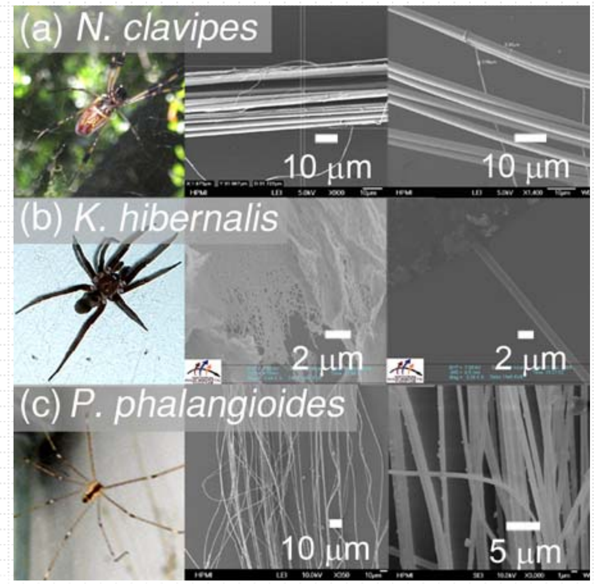
Spidroin 2

$(GPGGY\ GPGQQ)_3$ GPSGPGS A_{10}

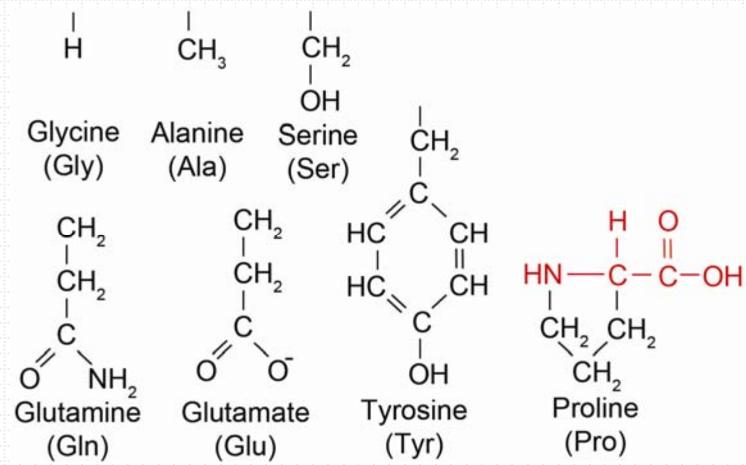
Silk	Spidroin 1	Spidroin 2
Dragline	+ + + +	+ +
Viscid	-	+ +

J.P. O'Brien, et al. Adv. Mater., ***10***, *1185 (1998)*

Spider silk used in this work

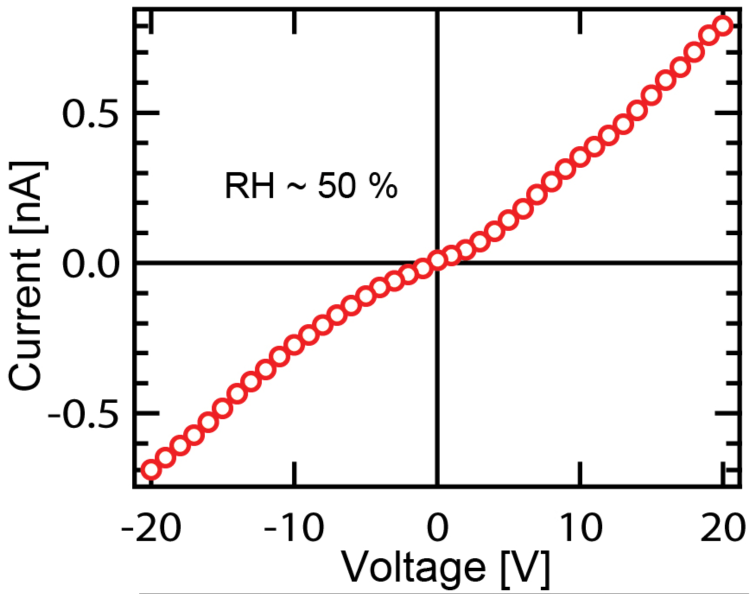


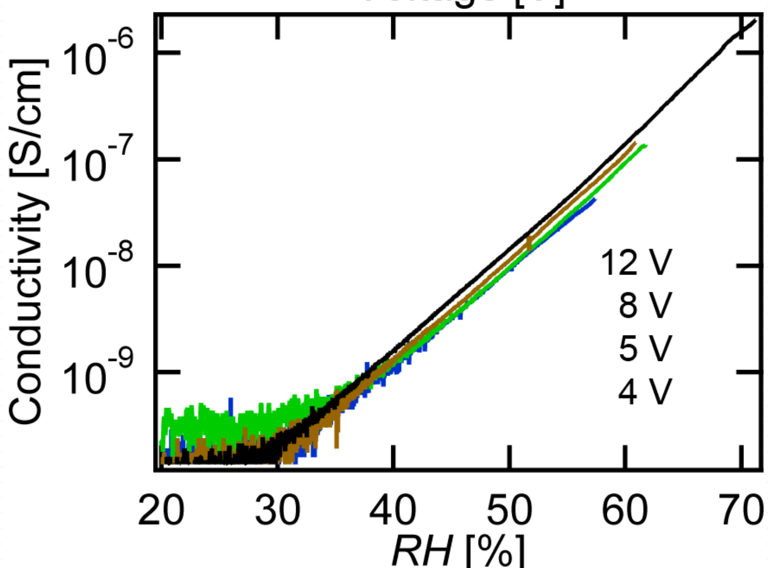
Amino acids present in spider silk



J.D. van Beek, et al. PNAS, ***99***, *10266 (2002)*

Humidity dependent conductivity of neat spider silk





Measurement was done on N. clavipes dragline silk.

- Highly insulating: σ = 44nS cm-1 (at 50% RH).
- Slight non-linearity in the I-V curve at lower voltages.
- Humidity activated behavior: $\sigma = \sigma_0 \exp(0.23RH)$

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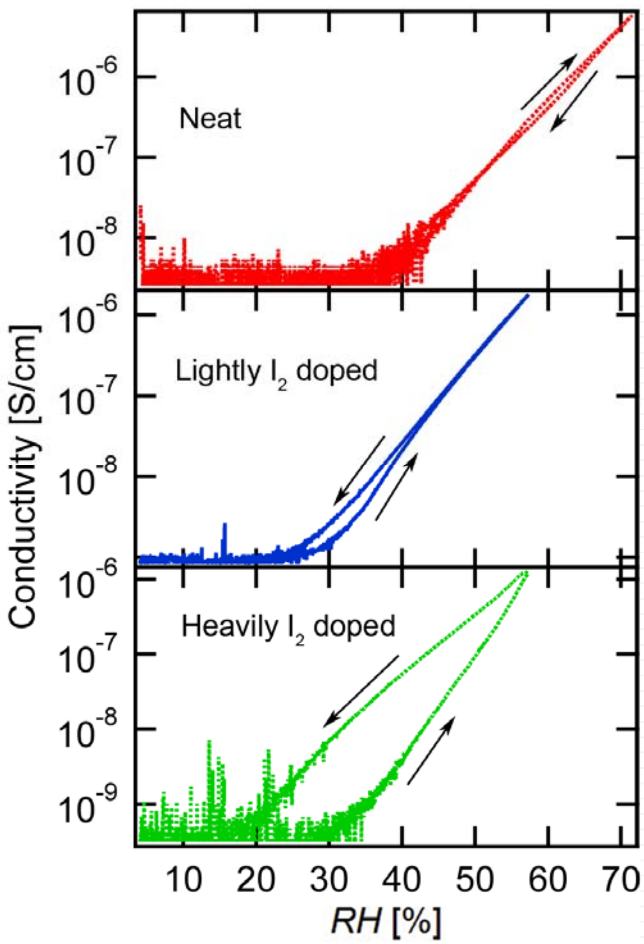
Effect of I_2-doping of spider silk: slight conductivity improvement



Procedure:

- Light I_2 doping: 25 C for 24 H. Then vacuum for 12 H. Original color restored after vacuum.
- Heavy I_2 doping: 70 C for 3 H. Then vacuum for 12 H. Color changed to deep-brown color permanently.

- Under ambient RH, conductivity increases ~ 600% for lightly I_2 doped sample.
- No additional conductivity increase for heavily I_2 doped sample.
- The cyclic response of neat silk is nearly reversible but I_2 doping caused more water retention resulting a hysteretic behavior.

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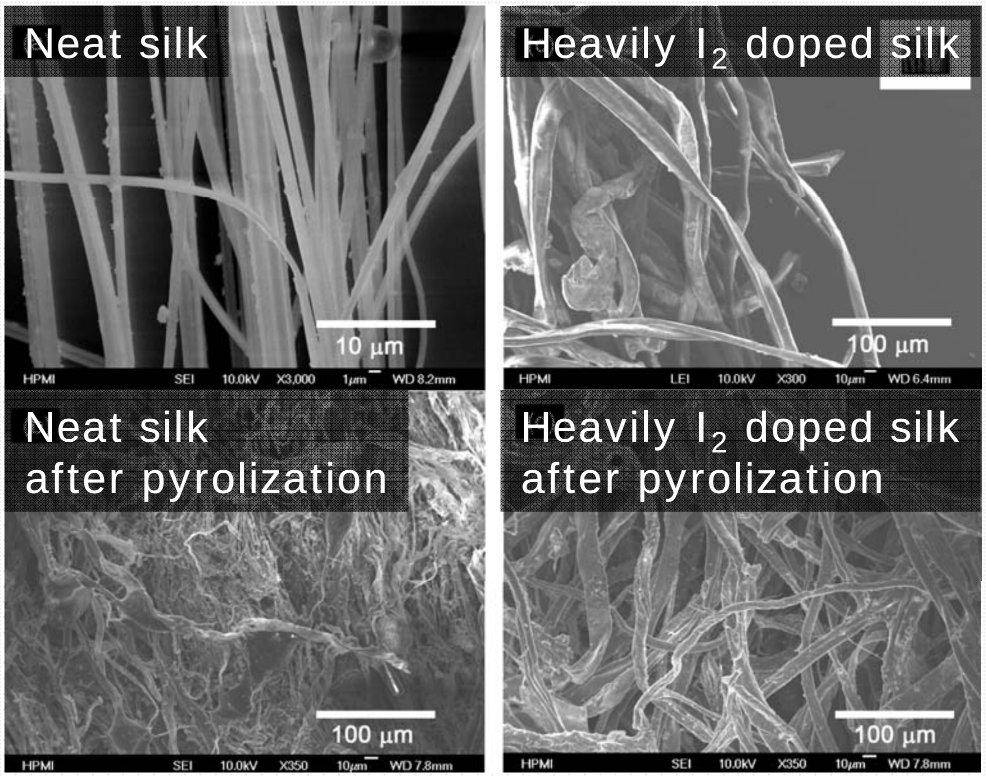
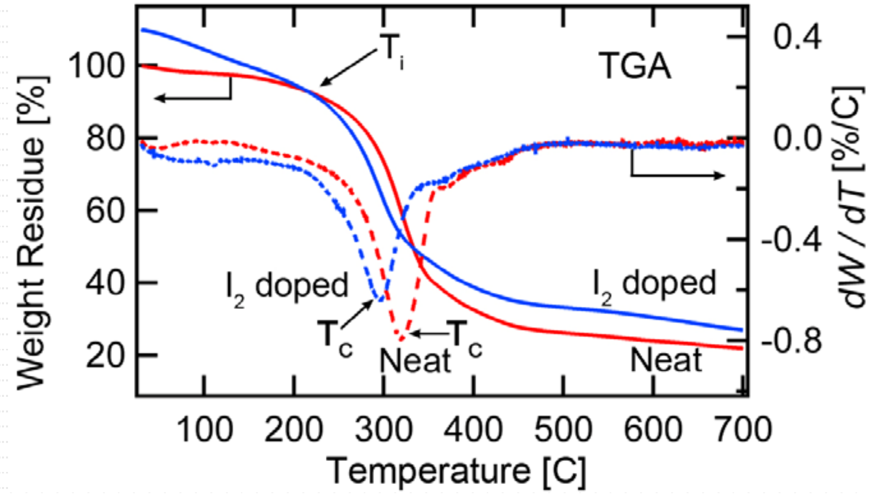
Effect of I_2-doping of spider silk: improved structure and carbon yield after pryolization

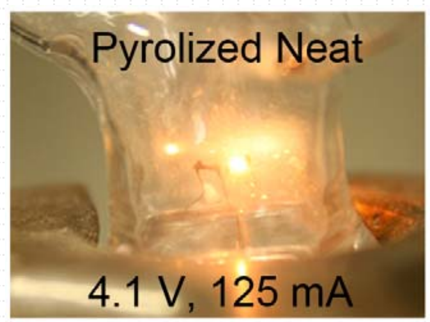
SEM analysis of pyrolized spider silk

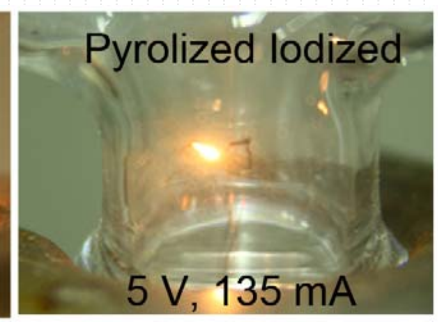


- Less disintegration and more flexible.



- Increased carbon yield of 7% for heavily I_2 doped sample.





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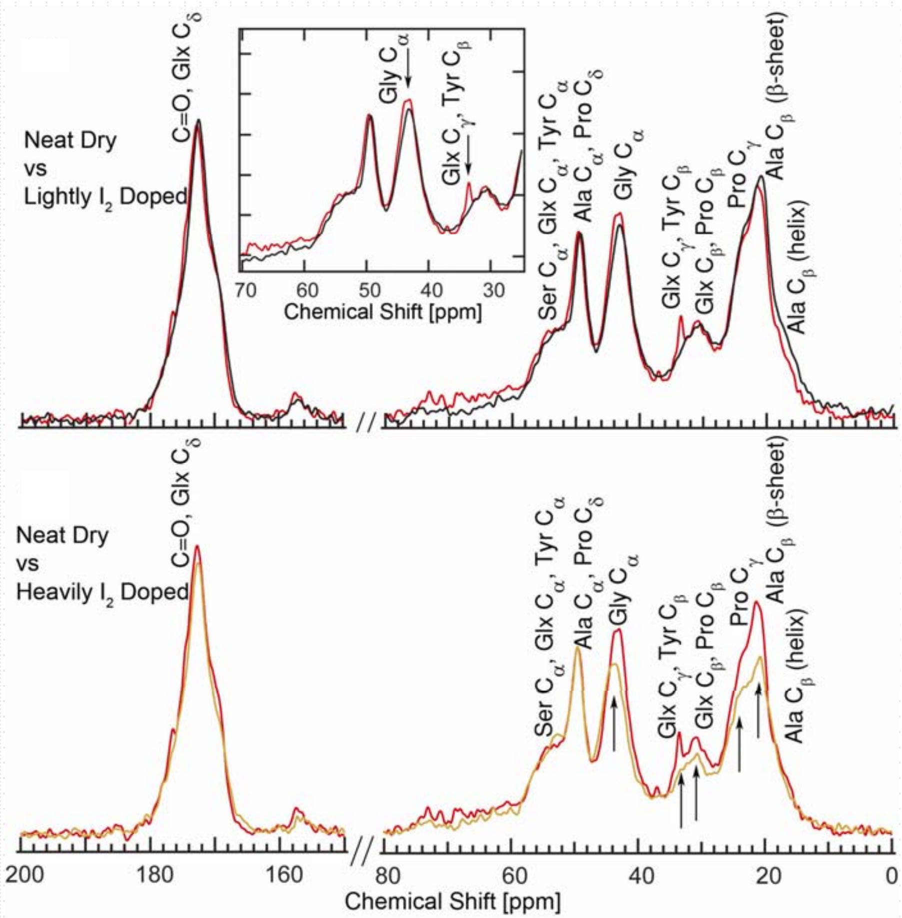
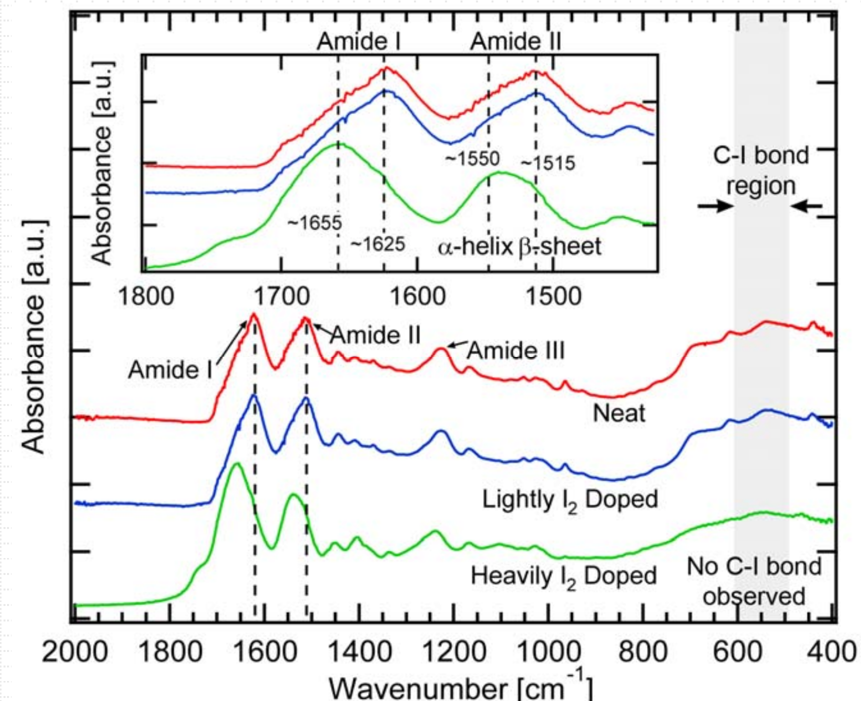
Effect of I_2-doping of spider silk: MAS-NMR and FTIR

$^{1}H - ^{13}C$ CP MAS-NMR of I_2 doped silk



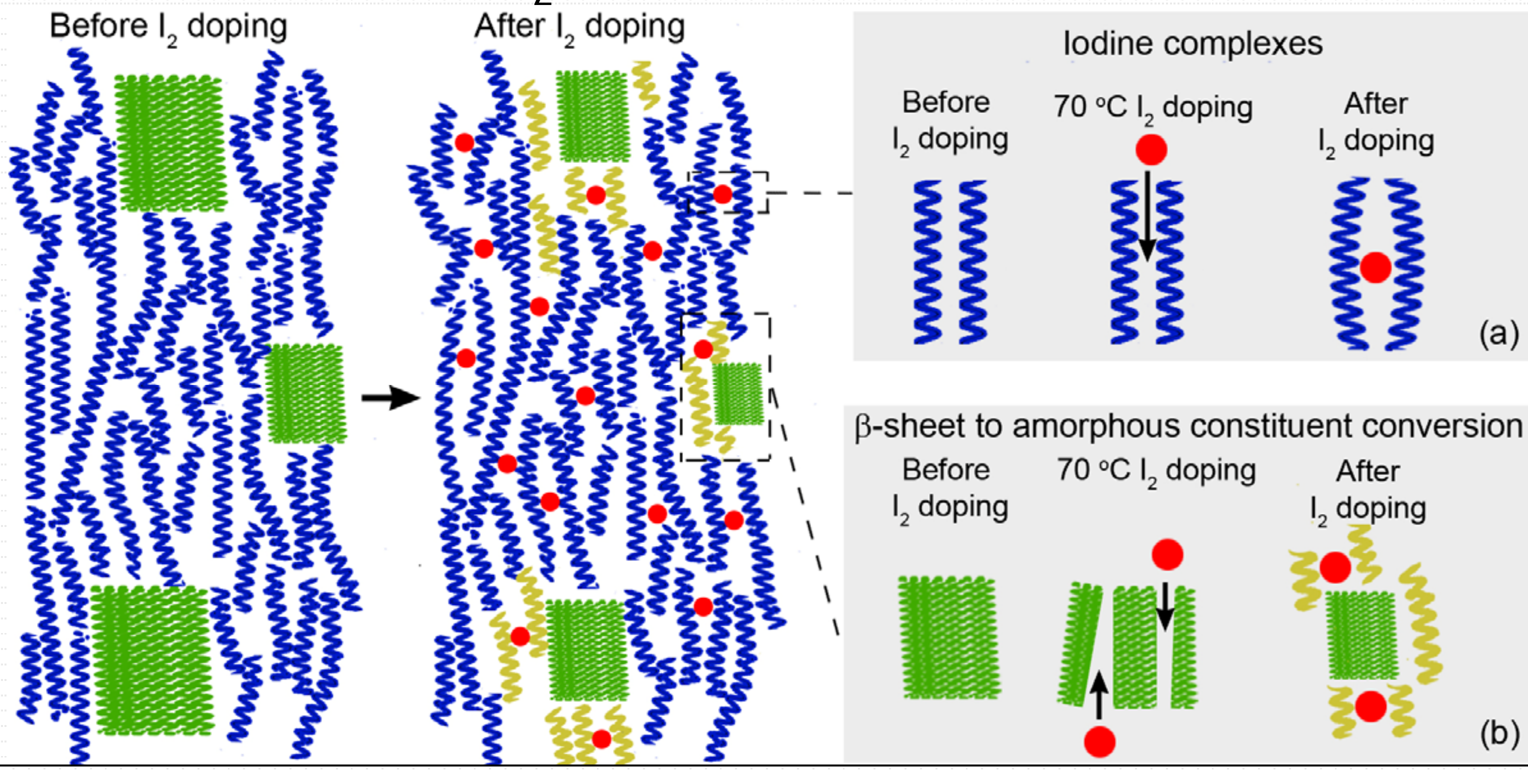
- Light I_2 doping only minimally introduces I_2 into amorphous region.
- Heavy I_2 doping introduces I_2 into both the amorphous and crystalline region.

FTIR of I_2 doped silk



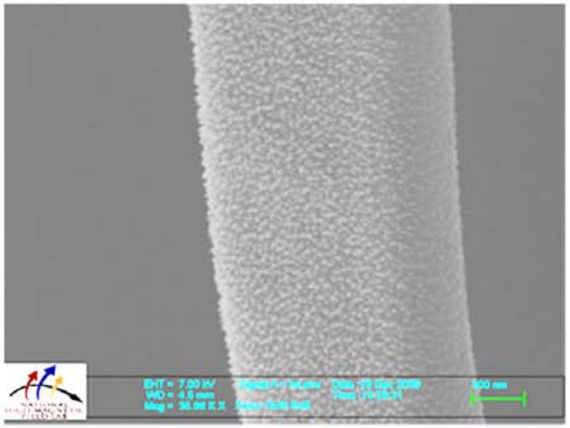
- No observable difference in FTIR spectra after light I_2 doping.
- Heavy I_2 doping reduces b-sheet peak and increases α-helix peak, indicating partial destabilization of some β-sheet into amorphous helices constituents.
- No C-I chemical reaction is observed. Diffusion process is more likely.

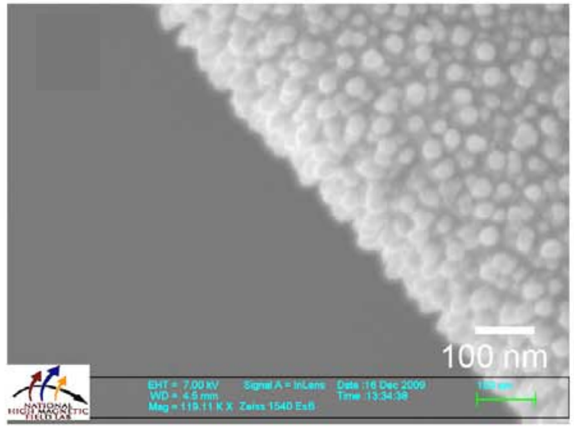
Qualitative Model of I_2-Silk Interaction

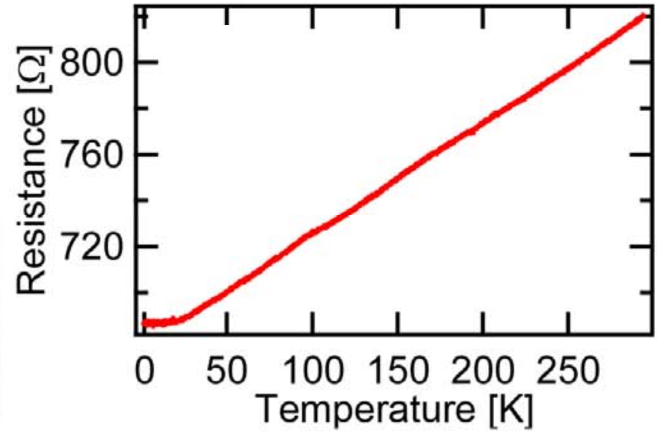


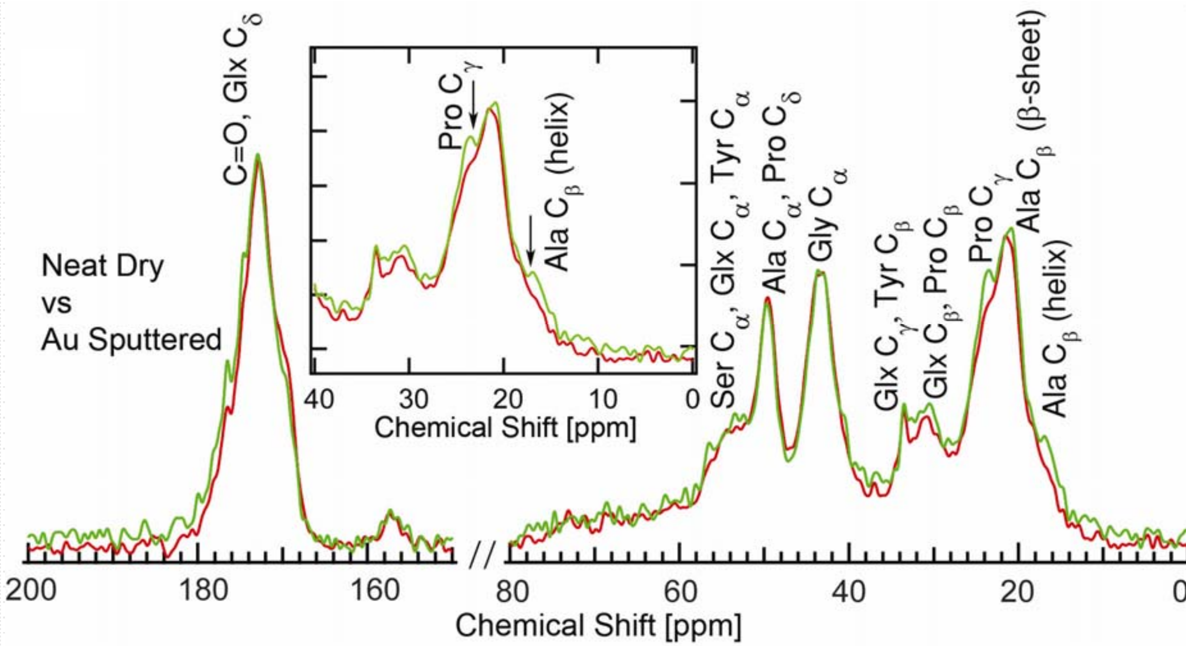
- Higher carbon yield: At 200 C, HI gas is produced → radicals generated → polymerization process accelerated → molecular weights of the components increased →higher amount of carbon is retained upon pyrolization.
- Better structure: Trapped iodine effectively change the interchain hydrogen bonding into iodine complexes that favor interchain van der Waals C-C interaction upon pyrolization.
- Minimal conductivity improvement: Only amorphous region is doped. The insulating b-sheet region limits the overall conductivity improvement.

Gold sputtered spider silk









- Gold adheres very well to the spider silk and robust down to ~260 mK.
- Spectra not strongly affected indicating that gold particle adheres mainly on the surface.
- Increase in intensity of Pro and Ala peaks suggesting good adherence of gold to silk via Pro and Ala sites.

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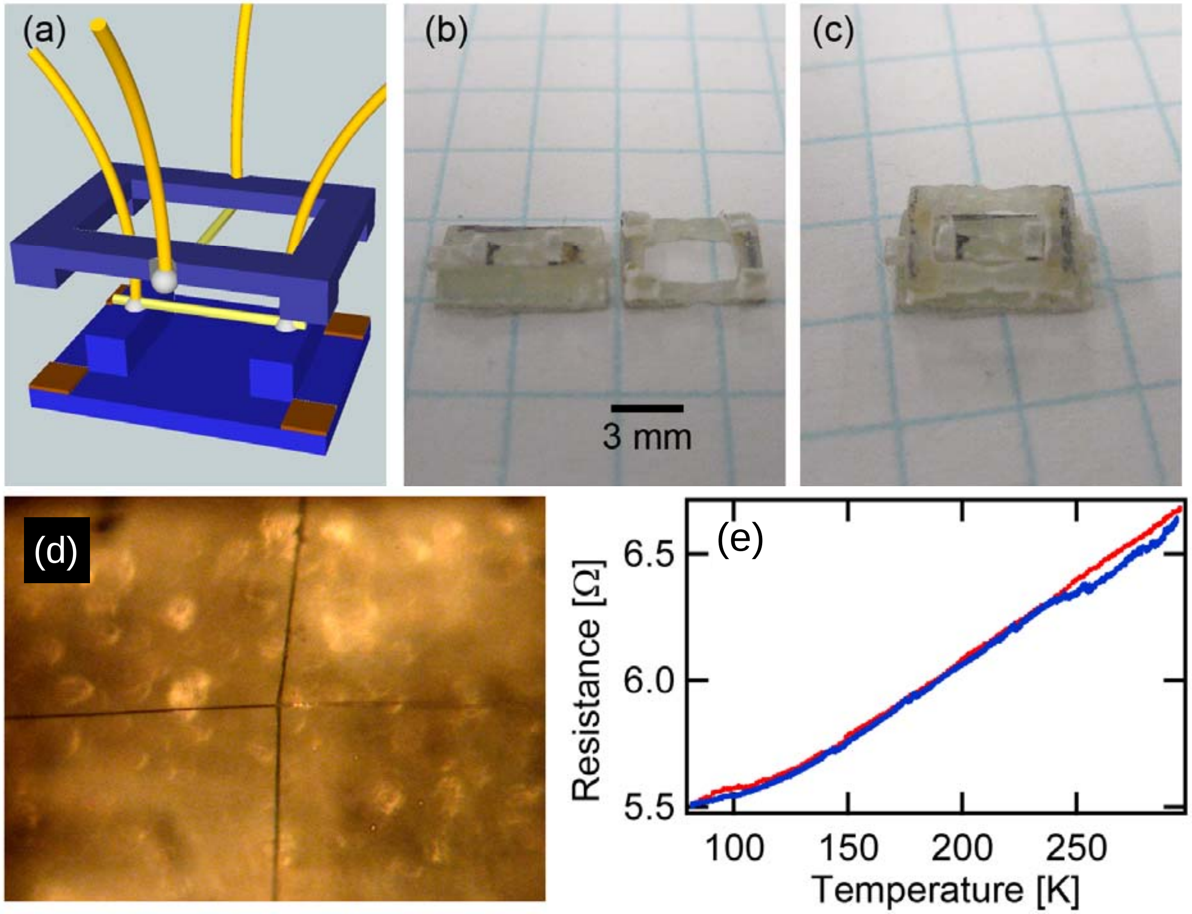
Electrical junctions

Gold sputtered silk cross junction

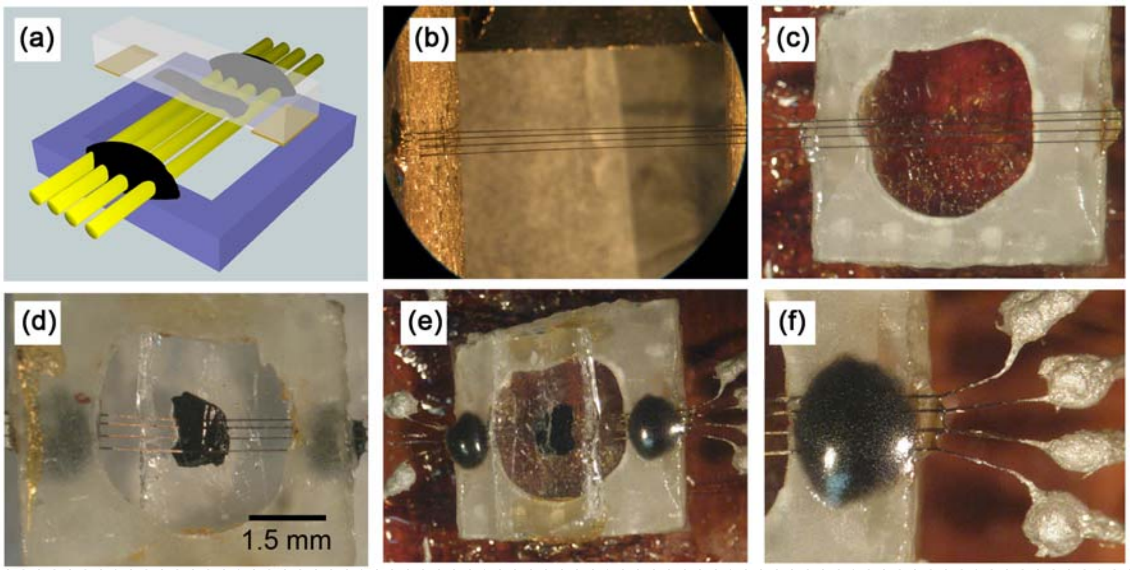


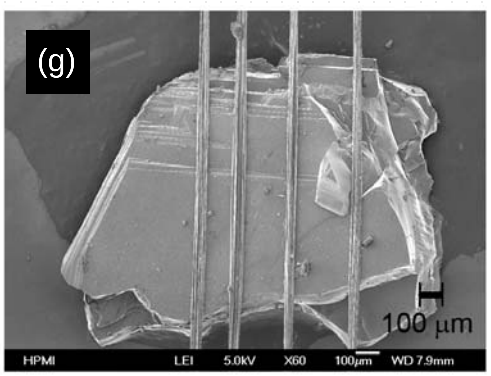
- The gold-sputtered silk fibers remained elastic.
- Robust cross-junctions under tension could be formed.
- In principle, for junctions involving p- and n-type coating, diode characteristics should be possible.

*E. Steven, et al. Sci. Technol. Adv. Mater **12**, 055002 (2011)*

Flexible and clean electrodes

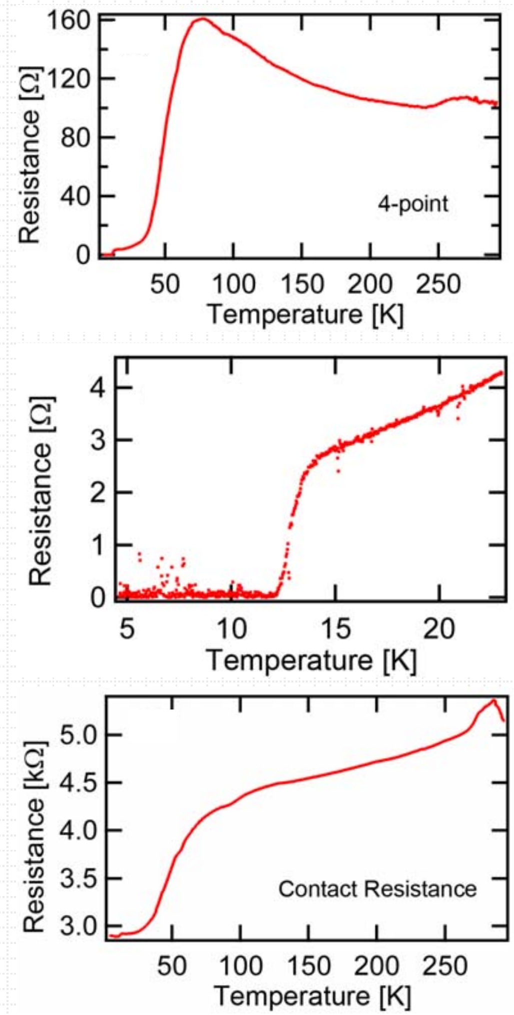
“Mandolin” configuration for transport characterization





- Flexible and clean pressure contact.
- Securing the silk fibers onto a G10 using Stycast 2850 is very important to prevent slipping.
- Robust down to ~4.3 K.
- Lower contact resistance at lower temperature.

κ-$(BEDT\text{-}TTF)_2Cu[N(CN)_2]Br$



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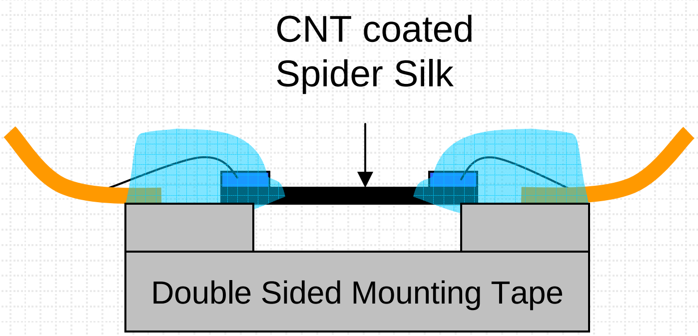
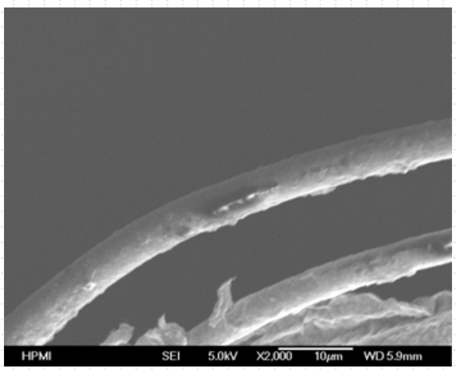
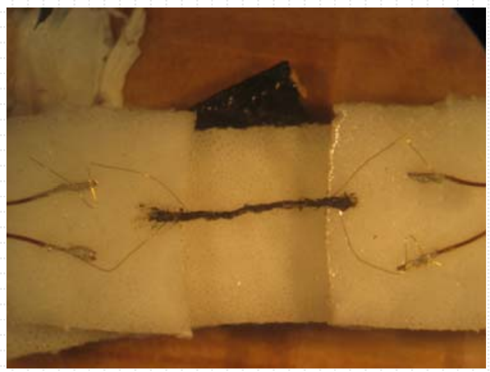
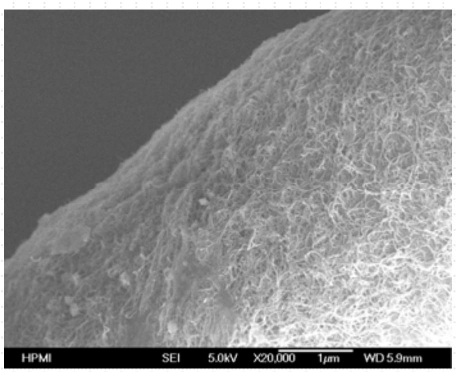
Future work: Carbon nanotube coated/doped spider silk

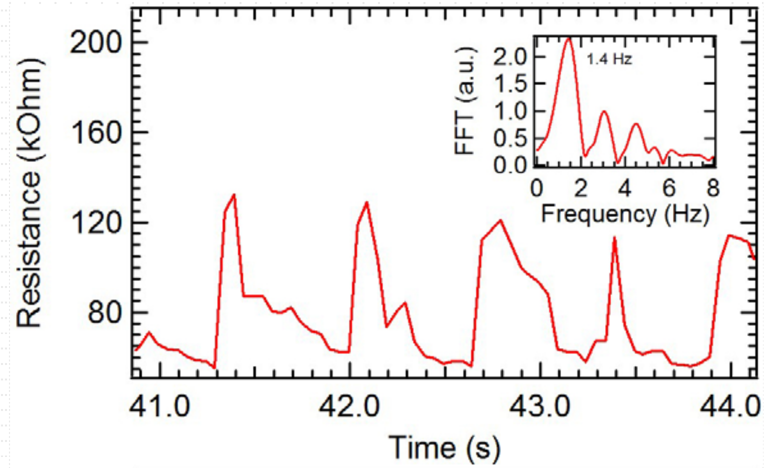


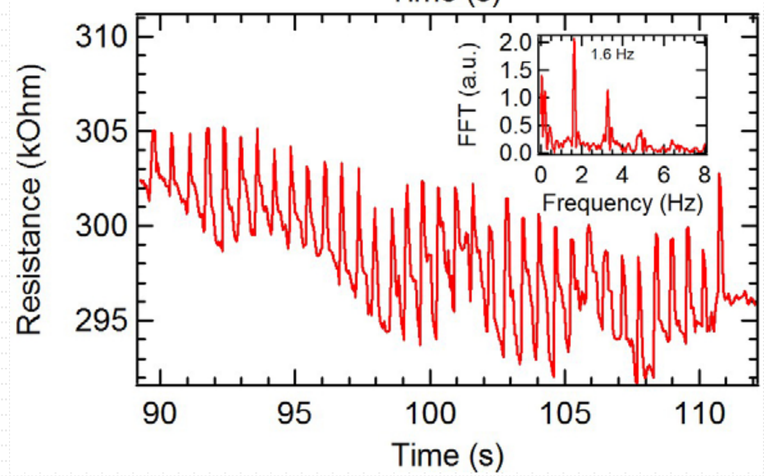
- Fairly uniform CNT-coating by dip-coating method.
- ΔR of ~ 100% can be reached initially. However, after multiple mount/peel-off cycle, the sensitivity is reduced. More work is needed to optimize the device.











Conclusion

- An excellent scaffolding for adding functions: biocompatible, air stable, flexible, strong.
- Good affinity/compatibility to many kind of nanoparticles or nanomaterials: gold particles, pentacene, carbon nanotubes, and many others.
- Complex chemistry of protein polymer gives wide possibility for tuning the biochemical/physical properties.
- Robust properties under ambient conditions.
- Challenge: High yield and high performance synthetic silk.

Conclusion

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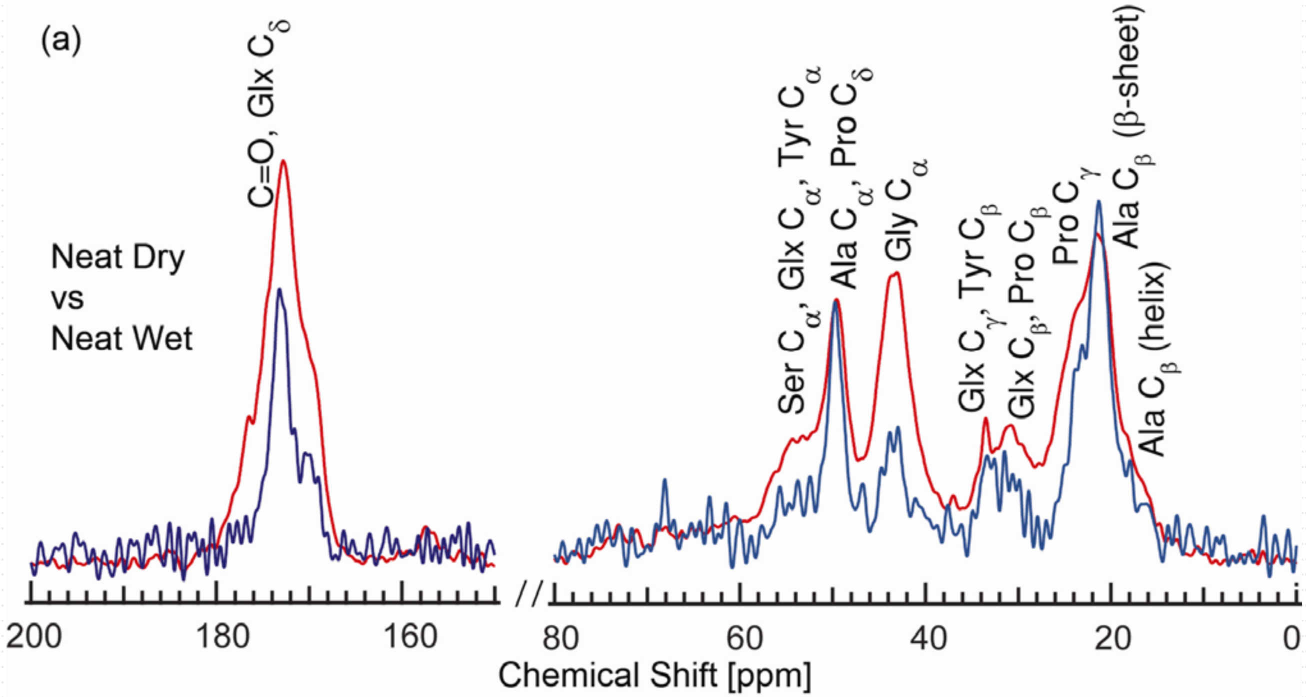
- Good affinity/compatibility to many kind of nanoparticles or nanomaterials: gold particles, pentacene, carbon nanotubes, and many others.
- Complex chemistry of protein polymer gives wide possibility for tuning the biochemical/physical properties.
- Robust properties under ambient conditions.
- Challenge: High yield and high performance synthetic silk.

Thank you

Appendix

MAS-NMR of dry vs wet neat spider silk



- Hydration decreases intensity of most peaks except Ala C_α and Ala C_β (β-sheet) which is located in the β-sheet blocks.
- Thought to be due to increasing mobility of the protein backbone and side-chain mobility with hydration [REF].
- Intensitiy drop is largest for Gly followed by Glx, Ser and Pro peaks.
- May suggests a sequential water absorbing mechanism which could be related to the observed activated behavior.

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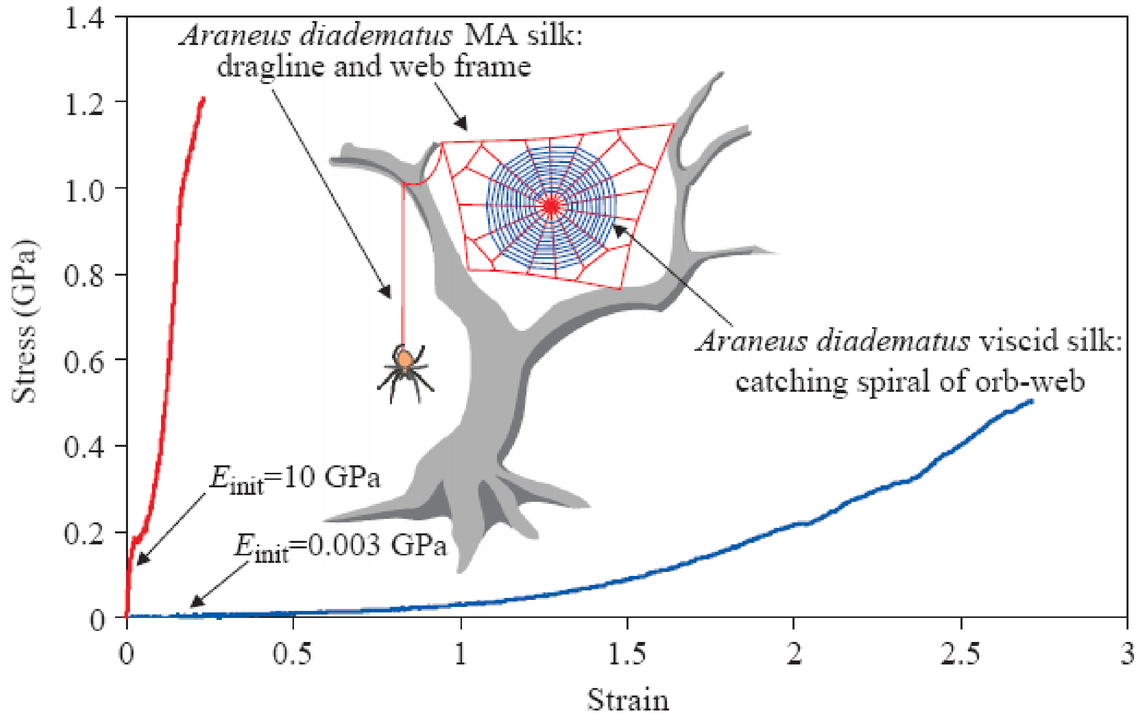
Mechanical properties



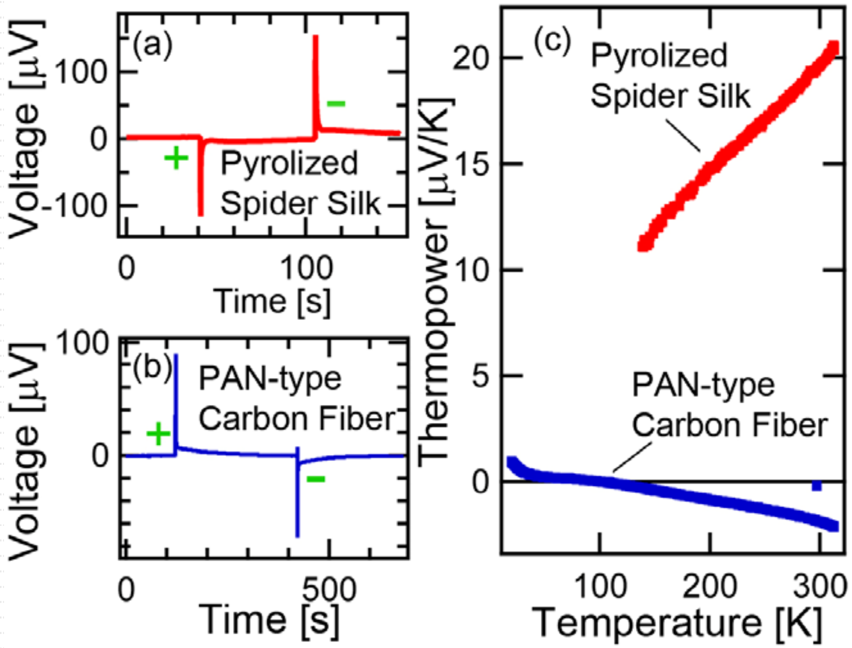
Although not as extensible as rubber and not as strong as Kevlar 49, spider silk is considered the **toughest** materials.

Material	Stiffness (GPa)	Strength (GPa)	Extensibility (%)	Toughness (MJ m^{-3})
Spider dragline silk	10	1.1	27	**160**
Spider viscid silk	0.003	0.5	270	**150**
Synthetic rubber	0.001	0.05	**850**	100
Kevlar 49	130	**3.6**	2.7	50

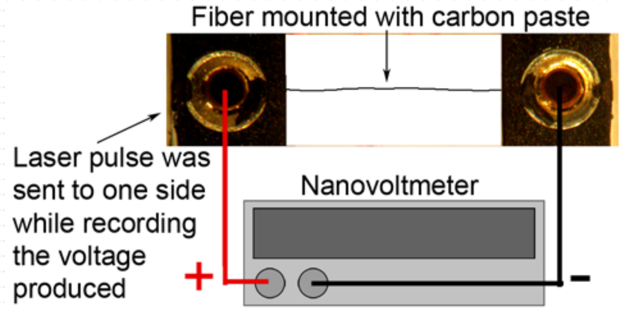
J.M. Gosline. J. Exp.Biol, 202, 3295 (1999)

Thermoelectric and incandescence of pyrolized spider silk

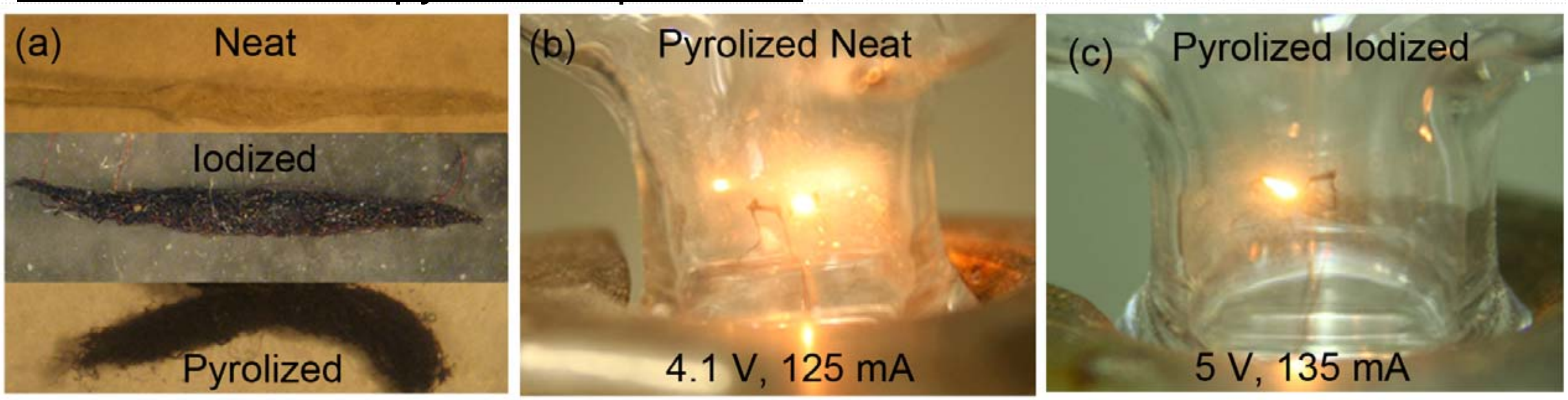
Thermoelectricity of pyrolized spider silk



- Pyrolized silk is a p-type semiconductor.
- The incandescence appeared to be conventional blackbody radiation.



Incandescence of pyrolized spider silk



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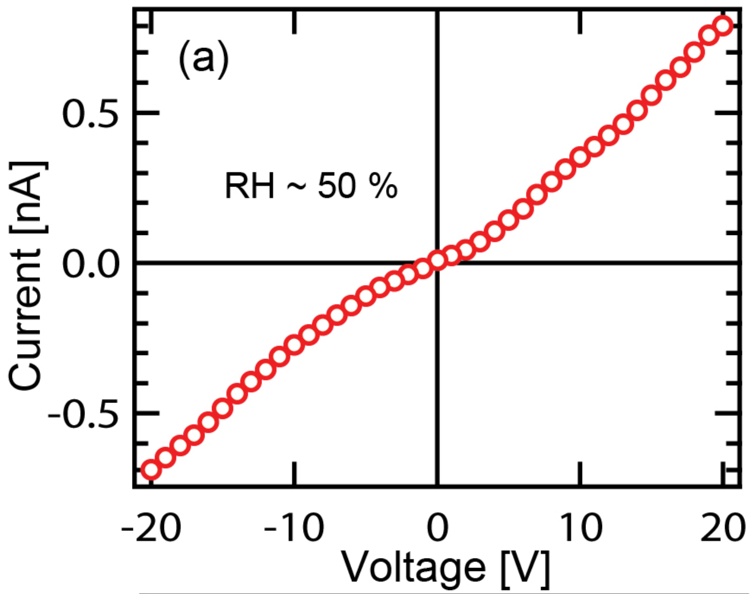
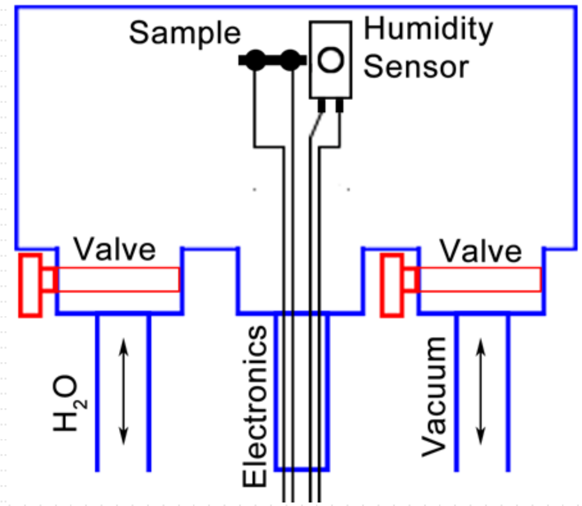
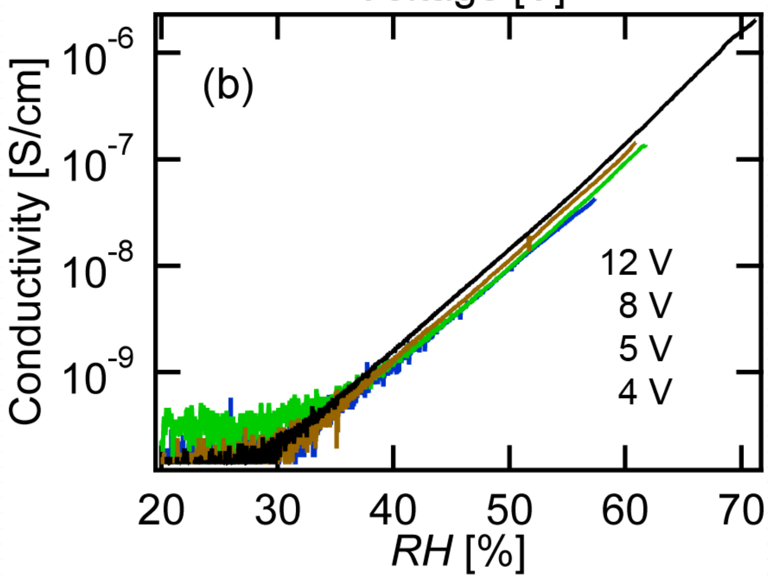
Humidity dependent conductivity of neat spider silk



Experimental setup





- Highly insulating:
  σ = 44nS cm-1 (at 50% RH).
- Slight non-linearity in the I-V curve at lower voltages.
- Humidity activated behavior:
  $\sigma = \sigma_0 \exp(0.23RH)$

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