Electrical Property Tuning in Self-Healing Polymeric Films via Controlled Silver Nanoparticle Deposition

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Motivation

Flexible electronics

- Sensors
- Wearable devices
- Electronic skin

Multifuncional materials

- Electrical properties
- Mechanical properties
- Biocompatibility
- Self-healing

- Simultaneous electrical performance and self-healing capability
- Achieving both high electrical performance and self-healing in flexible systems

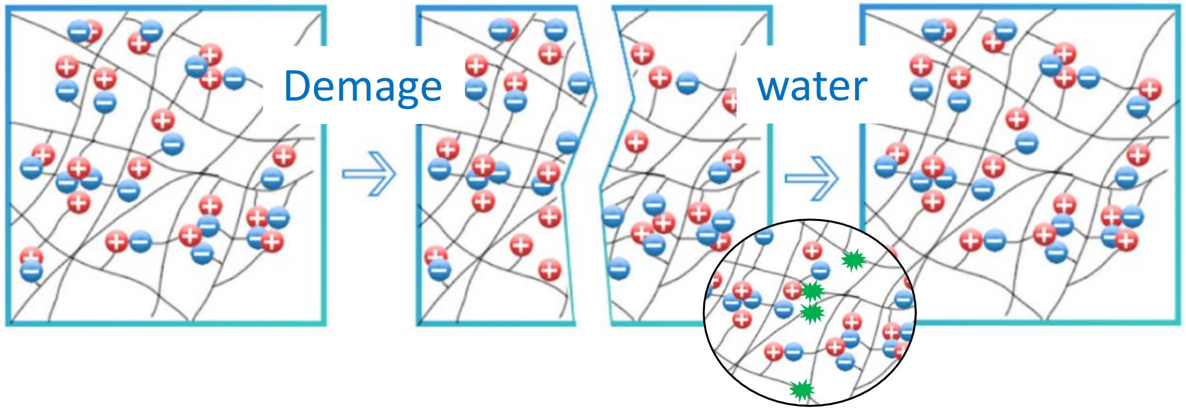
Modify electrical properties by implanting AgNPs in a polymeric matrix

Yang, J.C., Mun, J., Kwon, S.Y., Park, S., Bao, Z. and Park, S. (2019), Electronic Skin: Electronic Skin: Recent Progress and Future Prospects for Skin-Attachable Devices for Health Monitoring, Robotics, and Prosthetics (Adv. Mater. 48/2019). Adv. Mater., 31: 1970337. https://doi.org/10.1002/adma.201970337

LbL self-healing (SH) thin films

Self-Healing process

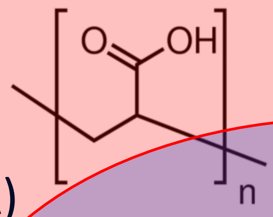
Small mechanical damages regenerates in the presence of water

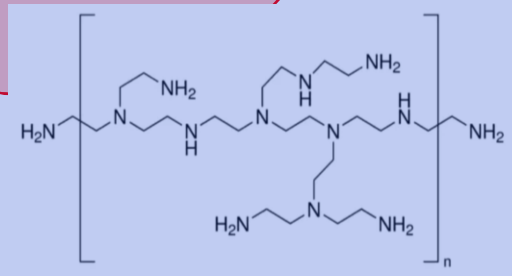


- Water in the hydrogel promoted the movement of polymer chains.
- Weak intermolecular interactions are necessary for SH.

Polyelectrolytes

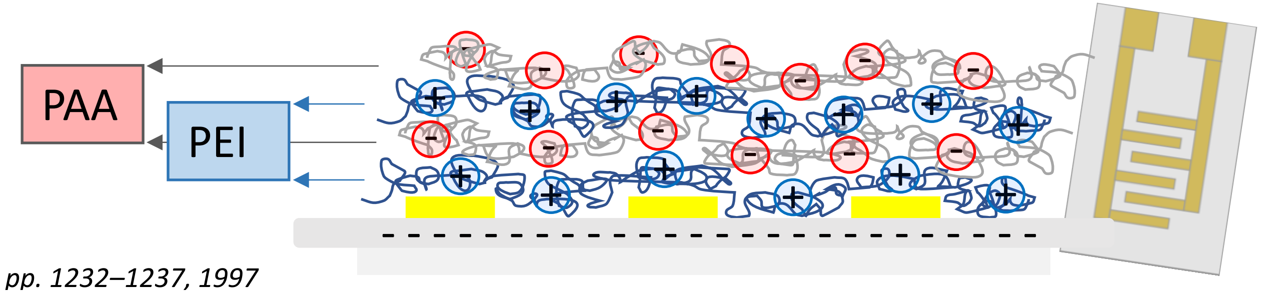
- Polyacrylic acid (PAA)
- Polyethyleneimine (PEI)





LbL (layer-by-layer) thin films

Self-assembly based on the charge compensation of polyelectrolytes

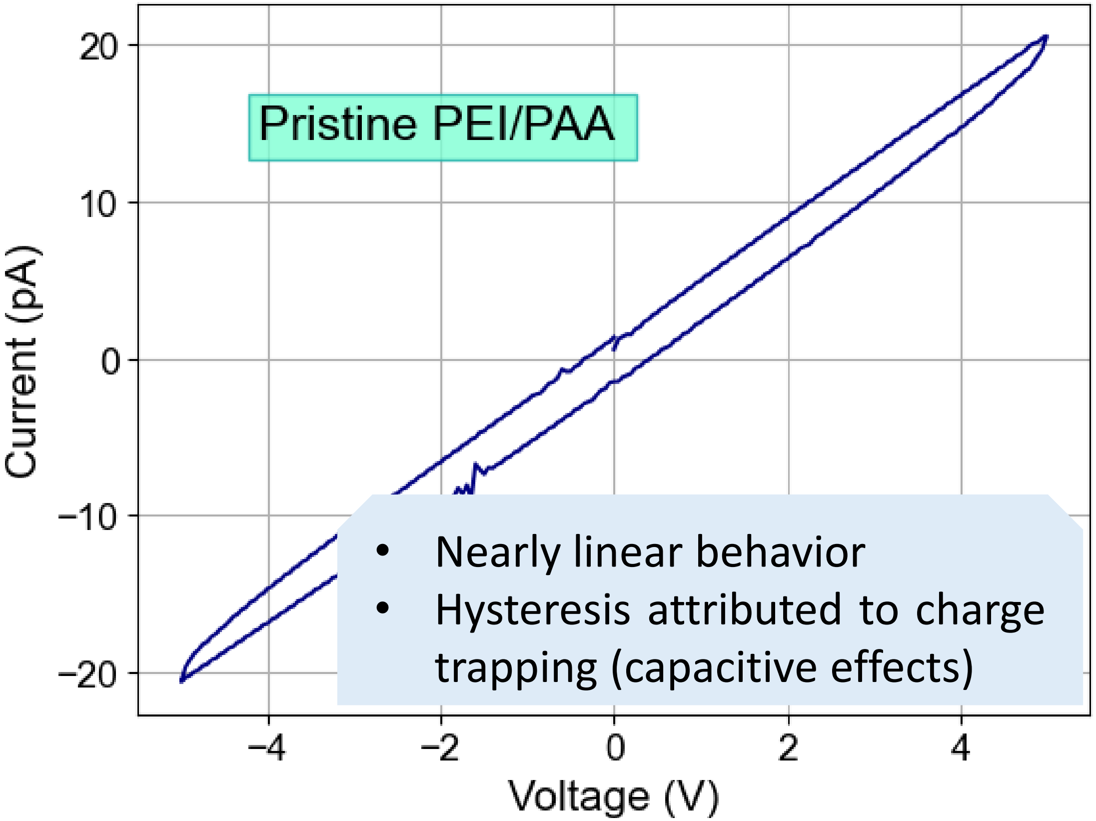


G. Decher, “Fuzzy nanoassemblies: toward layered polymeric multicomposites,” science, vol. 277, no. 5330, pp. 1232–1237, 1997
Zhang, Weiran, et al. "Recent achievements in self-healing materials based on ionic liquids: A review." Journal of Materials Science 55 (2020): 13543-13558.
X. Wang, F. Liu, X. Zheng, and J. Sun, “Water-enabled self-healing of polyelectrolyte multilayer coatings,” Angewandte Chemie International Edition, vol. 50, no. 48, pp. 11378–11381, 2011

LbL self-healing (SH) thin films

- Fexible and self-healing material

Dielectric Material



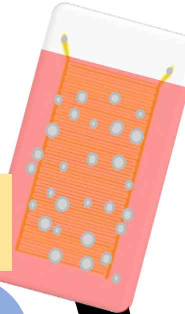
- Nearly linear behavior
- Hysteresis attributed to charge trapping (capacitive effects)

Matallic nanoparticles implantation

- Can increase conductivity and capacitance
- Modify charge transport mechanism
- Add new functionalities for the materials:
  - Memory properties

- Implant physically synthesized nanoparticles
- Direct interaction between polymer and nanoparticles

LbL+ AgNPs

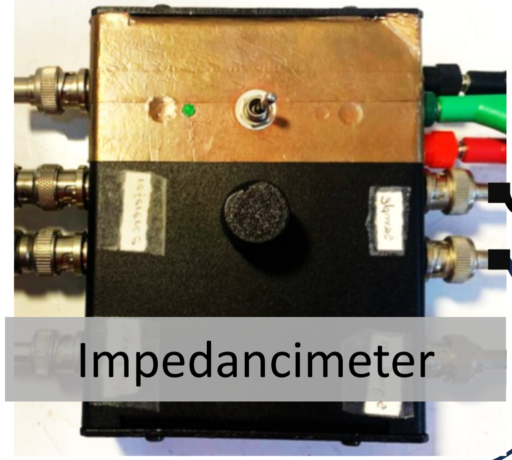


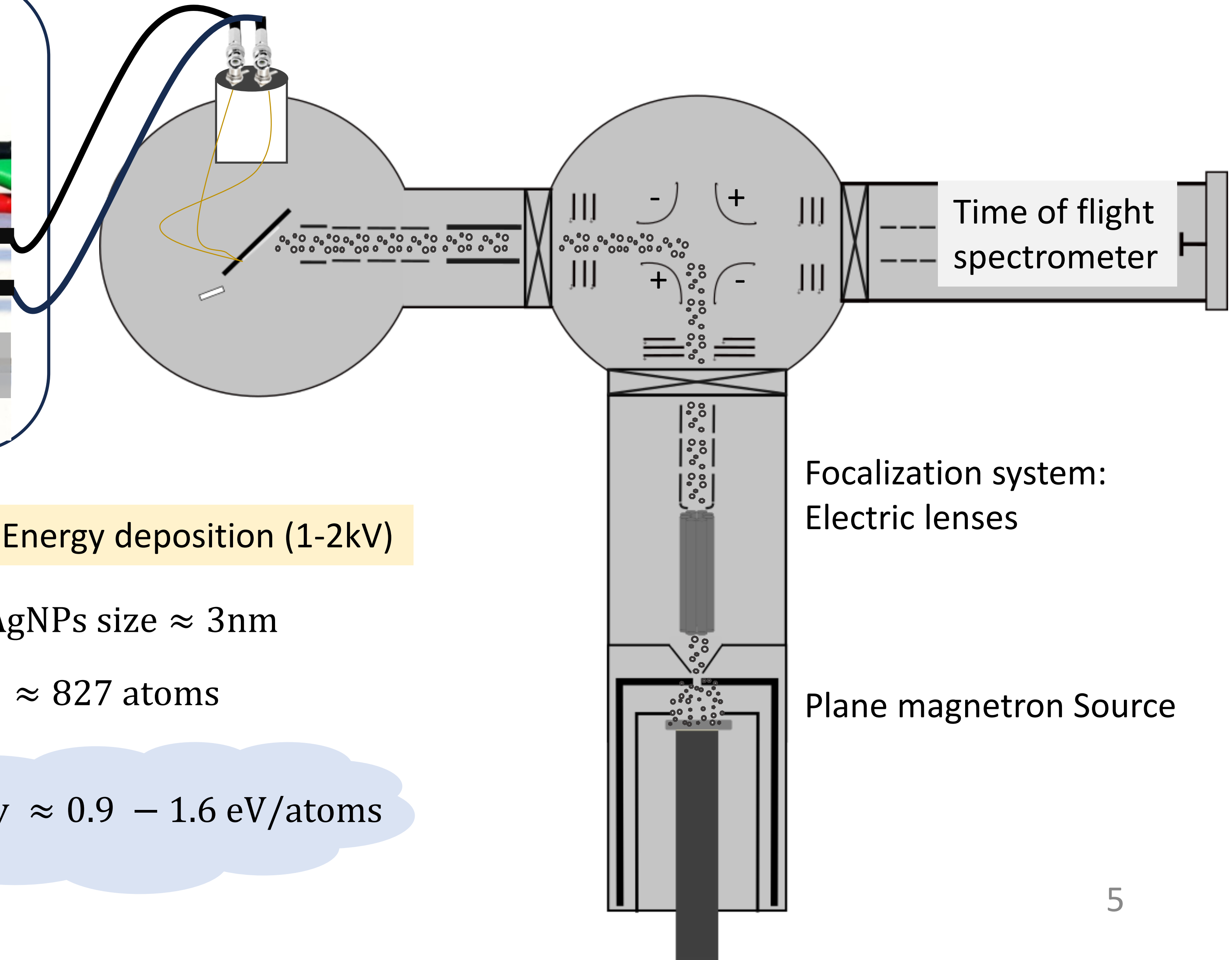
Study how AgNPs implantation changes electrical Properties of self-healing polimeric matrix

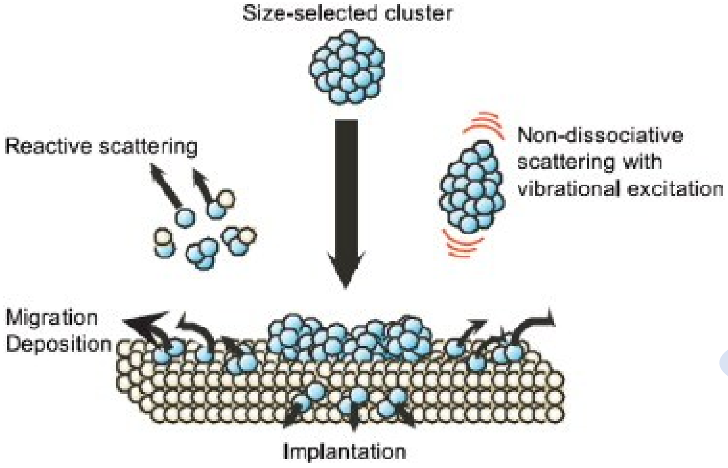
AgNPs deposition – Atomic Cluster Source

Ways of tracking deposition

Current sensor







High Energy deposition (1-2kV)

AgNPs size $\approx$ 3nm

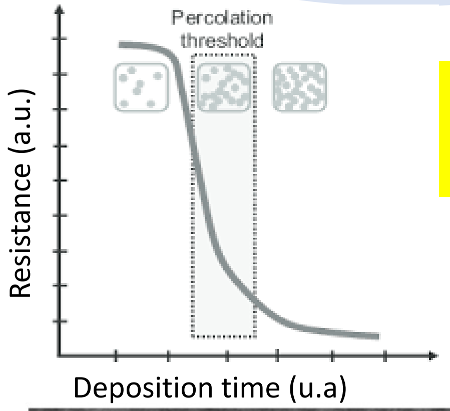
$\approx$ 827 atoms

Energy $\approx 0.9 - 1.6$ eV/atoms

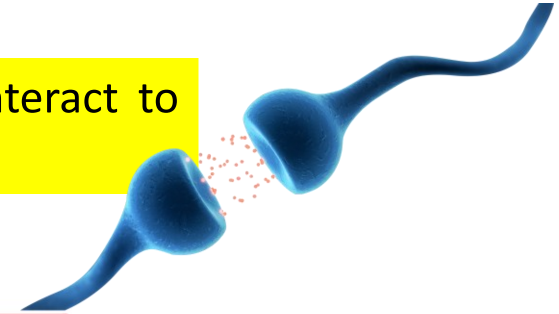
Popok, Vladimir N., et al. *Surface Science Reports* 66.10 (2011): 347-377.

Morphology of pristine AgNPs

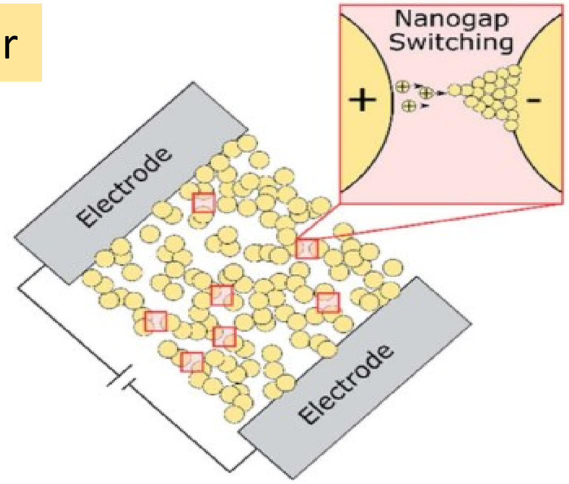
Deposited until begin of percolation treashhold



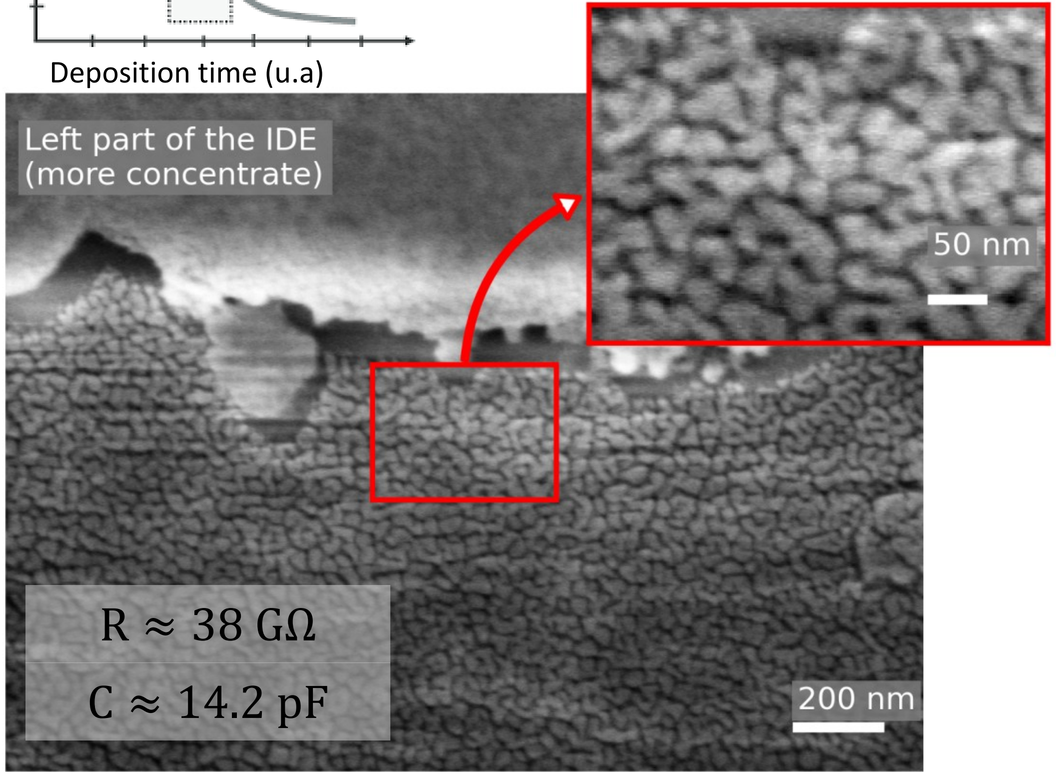
It is known that for NPs Interact to create conduction paths



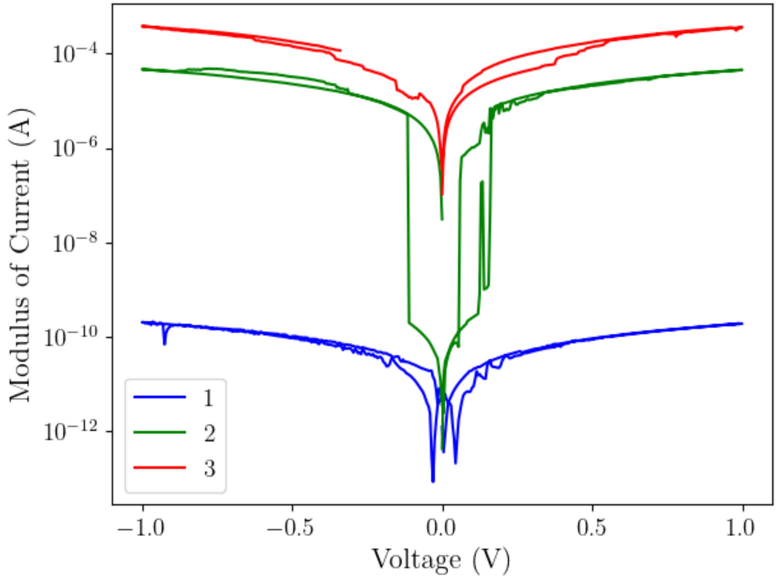
Neuromorphic behavior



Nanoscale Adv., 2022, 4, 3149

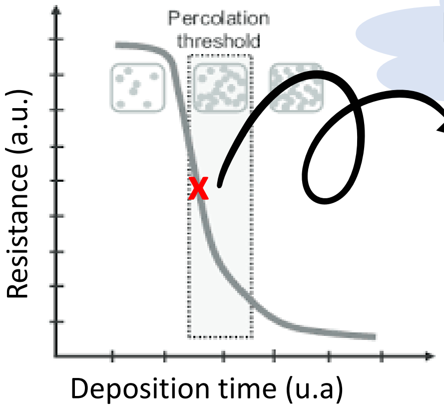


Upon applying a constant voltage, the film transitions to a percolated network.

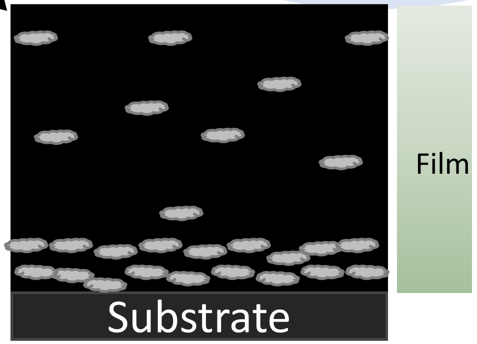


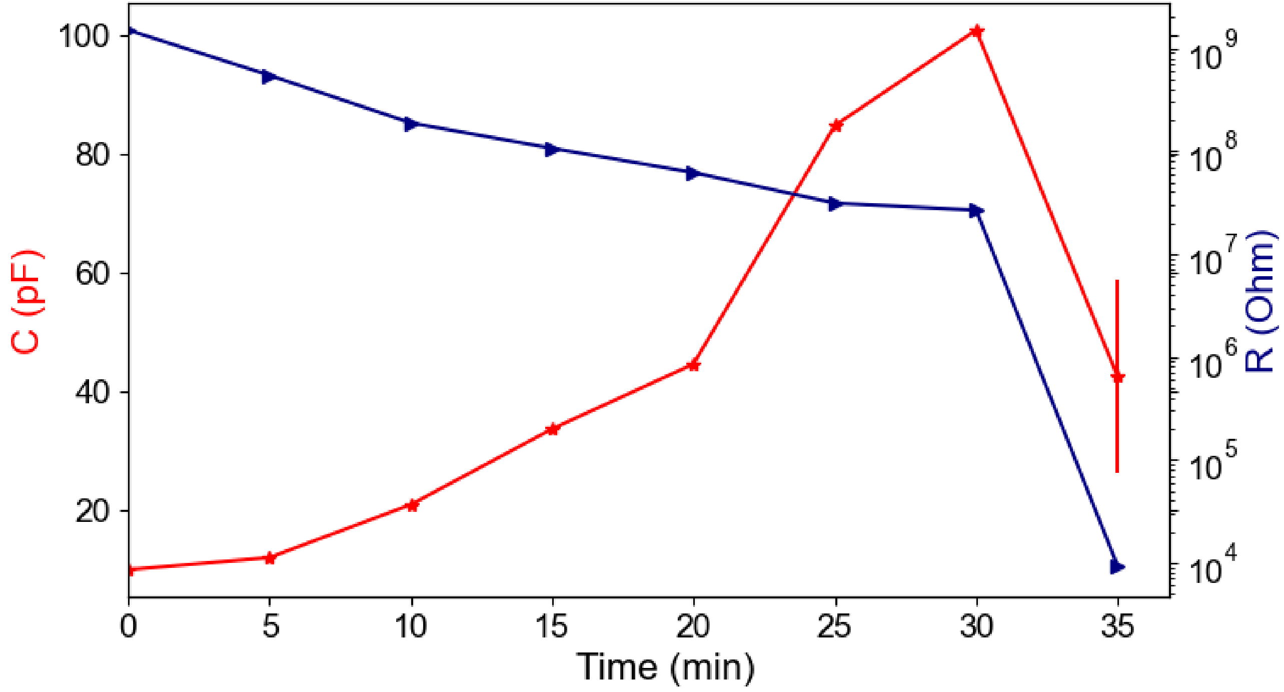
20 Voltage peaks of 10 V and -10V were applied

In-situ impedance monitoring – AgNPs+Polymer



Impedance was measured each 5 minutes

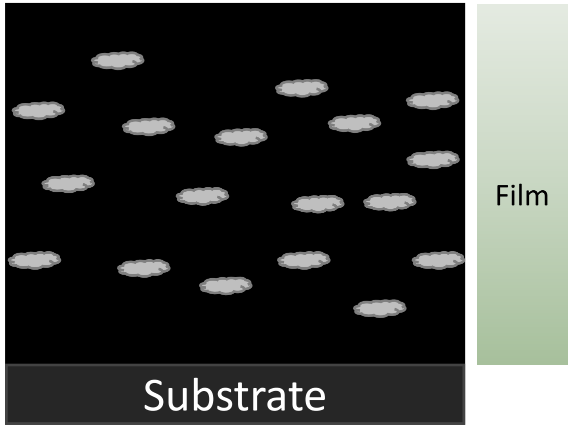




Kinetic evolution occurs after deposition.

Transition from a percolated to a non-percolated state after deposition

Surface migration?

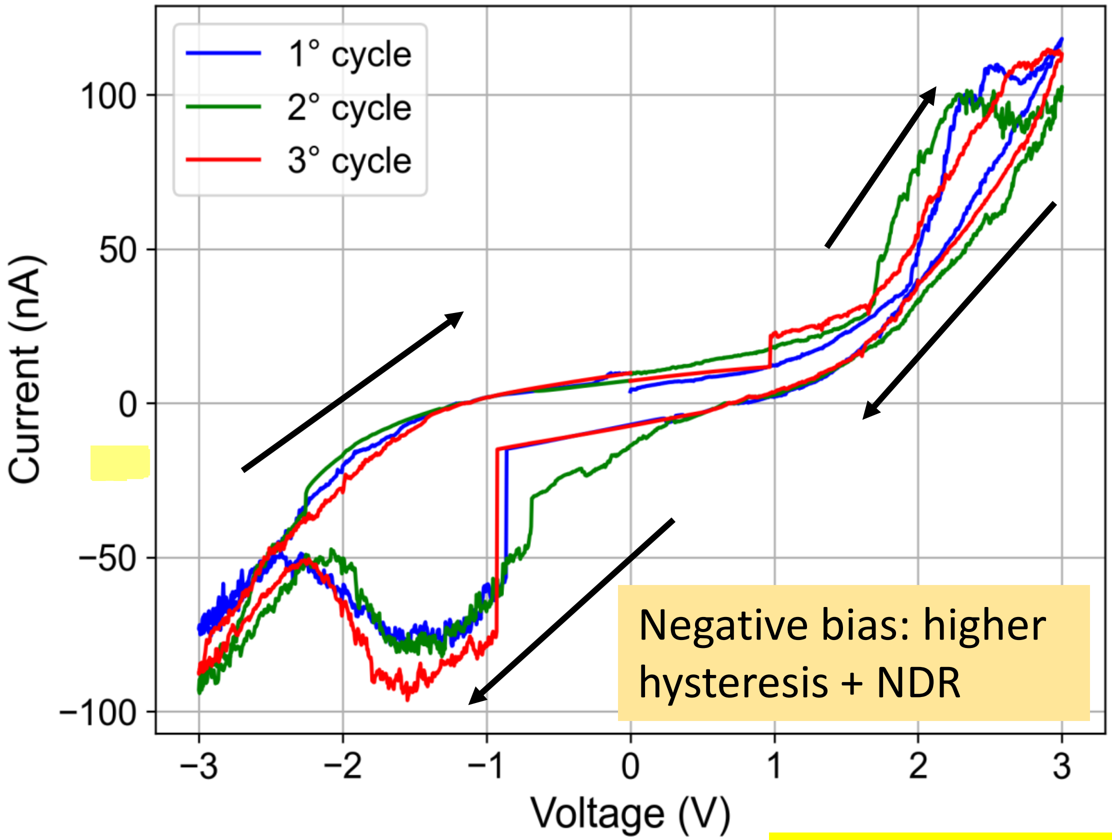


Interaction mechanisms remain unclear in the polyelectrolyte matrix

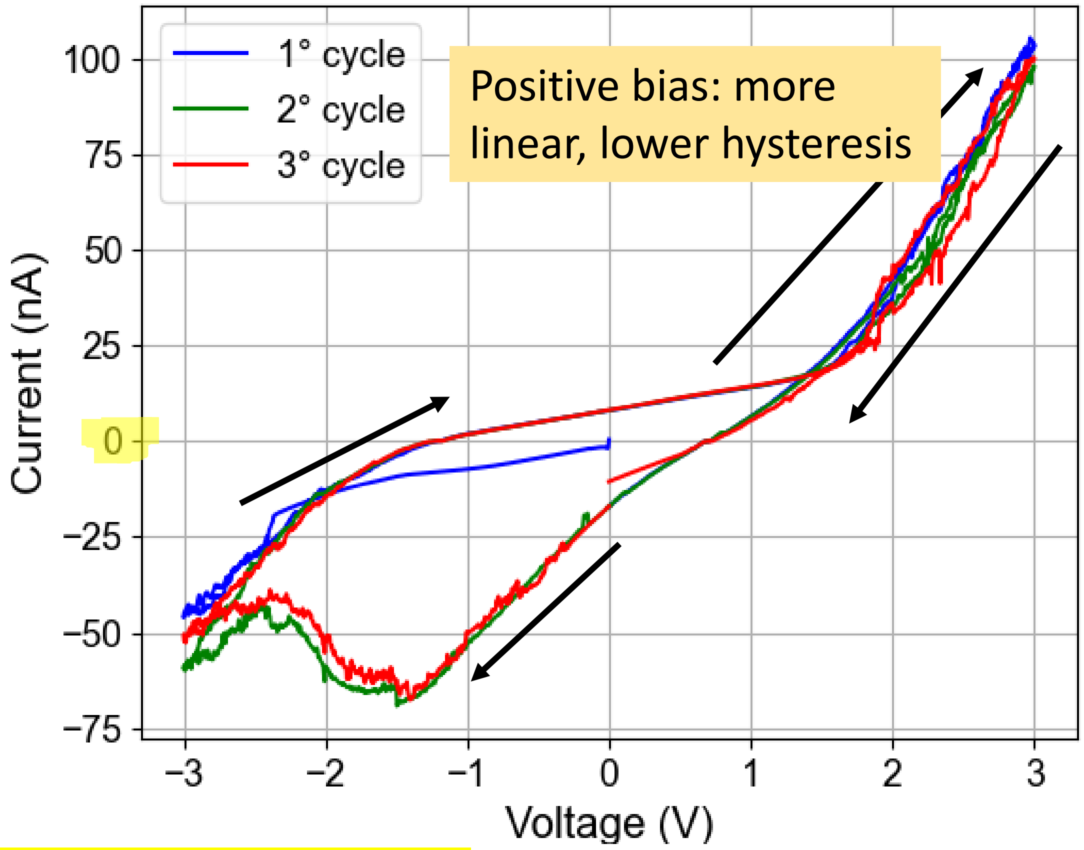
Electrical properties– AgNPs+Polymer

Cyclic IV curves

$0 \rightarrow V, \quad V \rightarrow -V, \quad -V \rightarrow 0$



$0 \rightarrow -V, \quad -V \rightarrow V, \quad V \rightarrow 0$

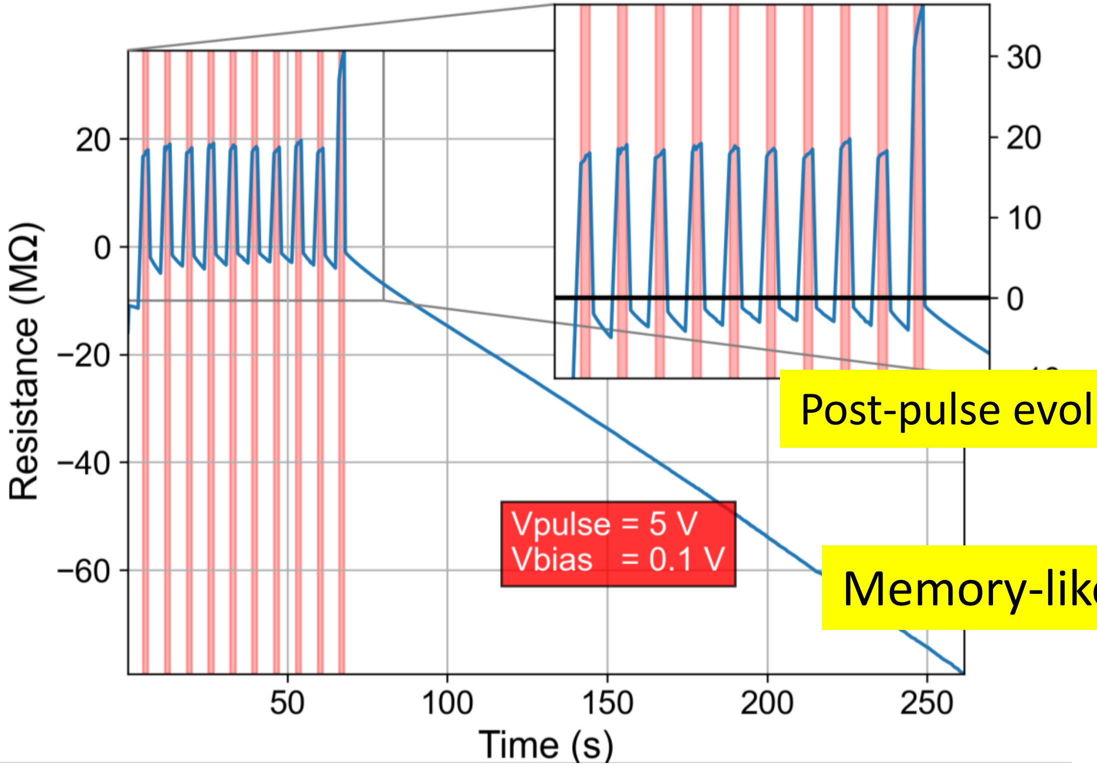


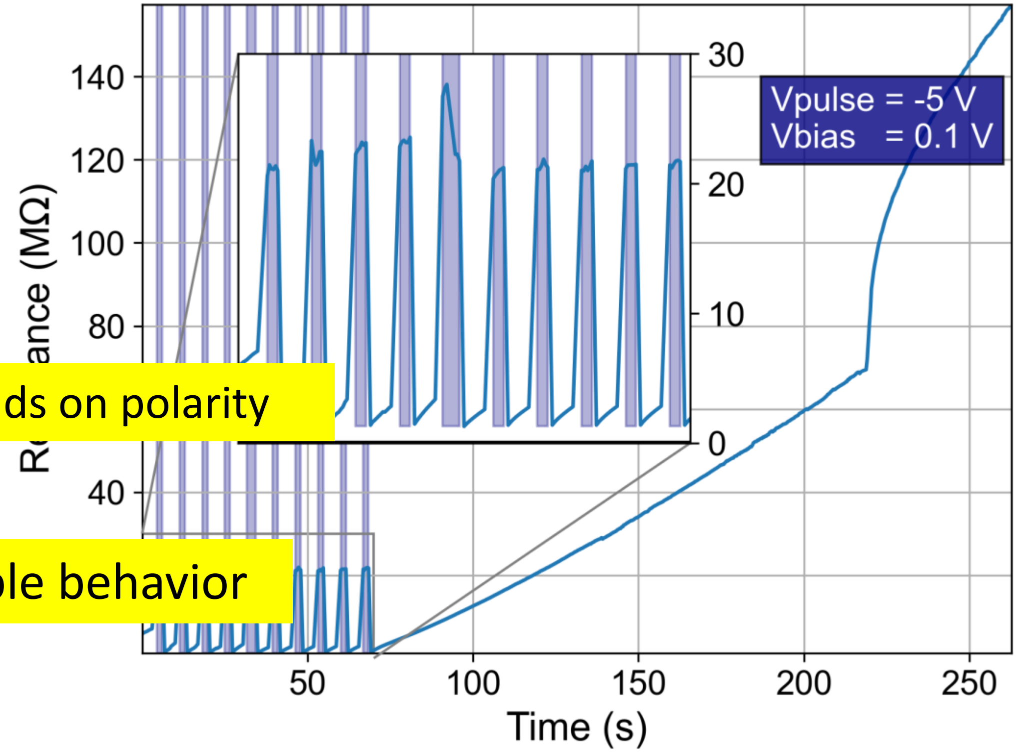
This asymmetry suggests a higher density of charge trapping under negative bias.

Electrical properties– AgNPs+Polymer

Voltage pulse experiment (±5 V)

- Two distinct resistance states are observed:
  - High-field state (±5 V pulses)
  - Low-field state (0.1 V read bias)





Post-pulse evolution depends on polarity

Memory-like, non-stable behavior

Resistance decreases further (more negative) under read bias

Resistance increases under read bias

Summary: Toward mechanism understanding and control

AgNP–polyelectrolyte films show dynamic electrical behavior.

- The polymer modifies nanoparticle interactions
- Conductive pathway formation I not trivial
- The system is not stable, relaxation occurs immediately after voltage application

Voltage pulses induce polarity-dependent resistive states.

The system exhibits polarity-dependent resistive switching.

Perspectives

- Clarify transport mechanisms:
  - Charge trapping at AgNP/polymer interfaces
  - Ionic motion in the polyelectrolyte matrix
  - Field-induced nanoparticle rearrangement
- Investigate time-dependent evolution (stability / relaxation effects).
- Correlate morphology (SEM) with electrical response.
- Improve stability and reproducibility of resistive states.

Nanoparticle incorporation in self-healing matrices as a strategy to enhance functionality for soft electronics

Next steps

- Vary deposition energy to analyze dispersion effects
- Additional electrical analysis:
  - Temperature-dependent I–V (activation vs tunneling)
  - Sweep rate dependence (to assess trapping dynamics)
- Establish structure–property relationships (electrical vs. morphology)

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Acknowlegments

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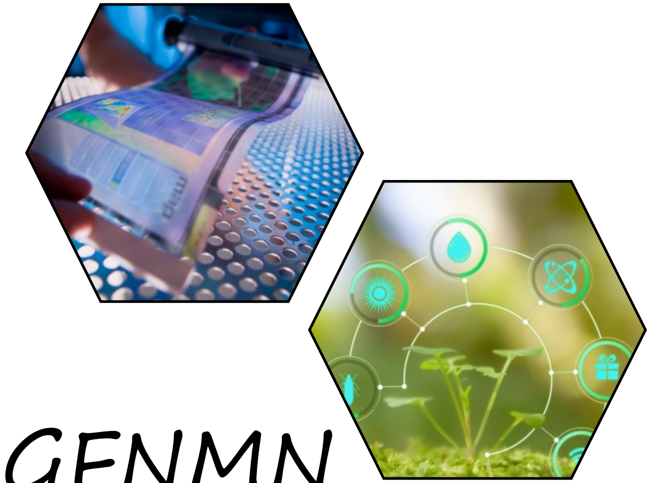
IFGW Applied Physics



GFNMN

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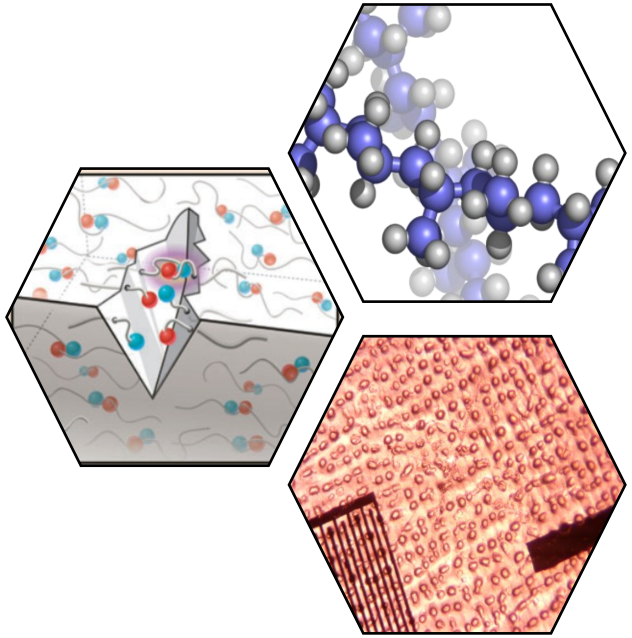

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