14th EUROPEAN CONFERENCE ON THERMOELECTRICS

Thermoelectric properties of PEDOT nanocomposites with electrochemically tuned oxidation state

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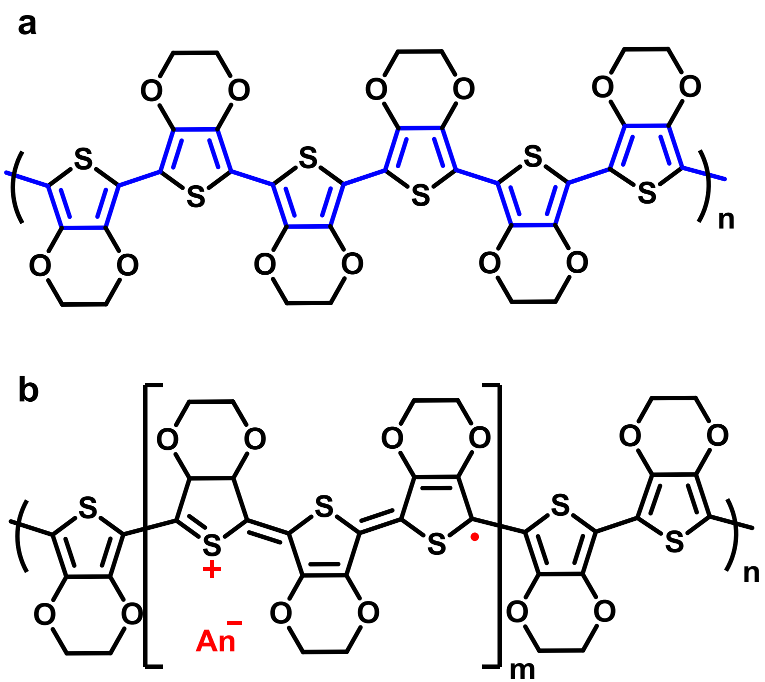
Poly(3.4-ethylendioxythiophene)
PEDOT



An⁻ = Tos⁻, Cl⁻, PSS⁻, ecc

Interesting Features

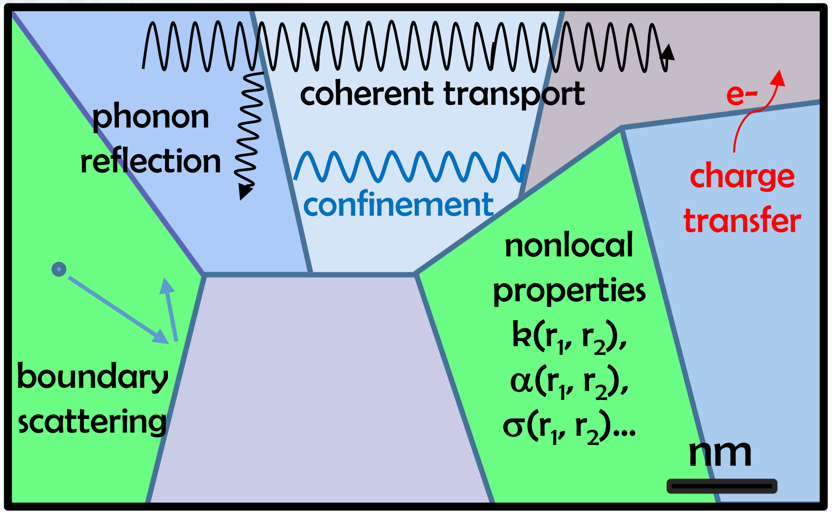
- Low thermal conductivity
- Medium-high electrical conductivity
- Easy processability
- Tunable electronic properties
- Adaptability to flexible substrate
- Environmental stability

B. Russ, et al. *Nat. Rev. Mater.*, 2016, **1**, 16050.

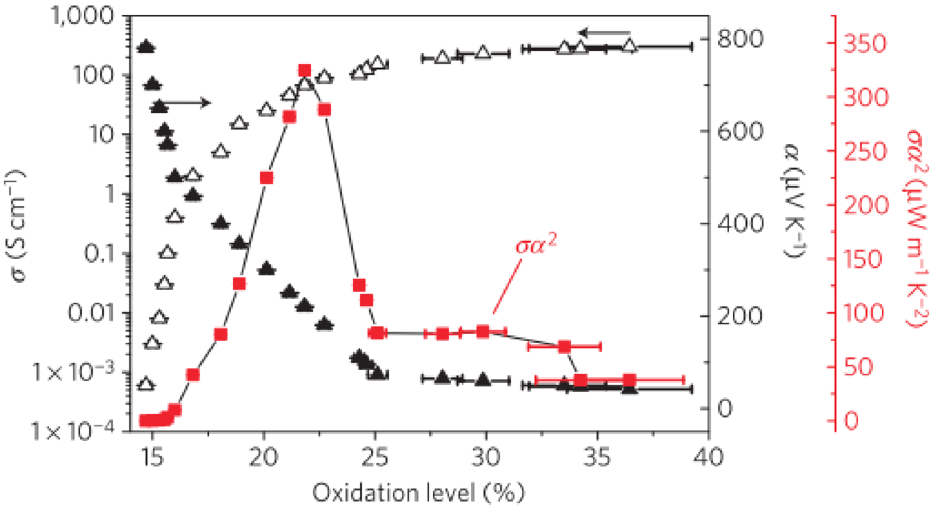
Performance Implementation Strategies

Nanostructuration

Inorganic Material Inspired Strategies



Majumdar, A. *Science*, 2004, **303**, 777–8



O. Bubnova, et al. *Nat. Mater.*, 2011, **10**, 429–33.

Conjugated Polymer Tailored Strategies

- Secondary Dopants Treatment
- Oxidation Level Tuning
- Counterion Variation

Oxidation Level Tuning: How to deal with PEDOT?

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OXIDATION

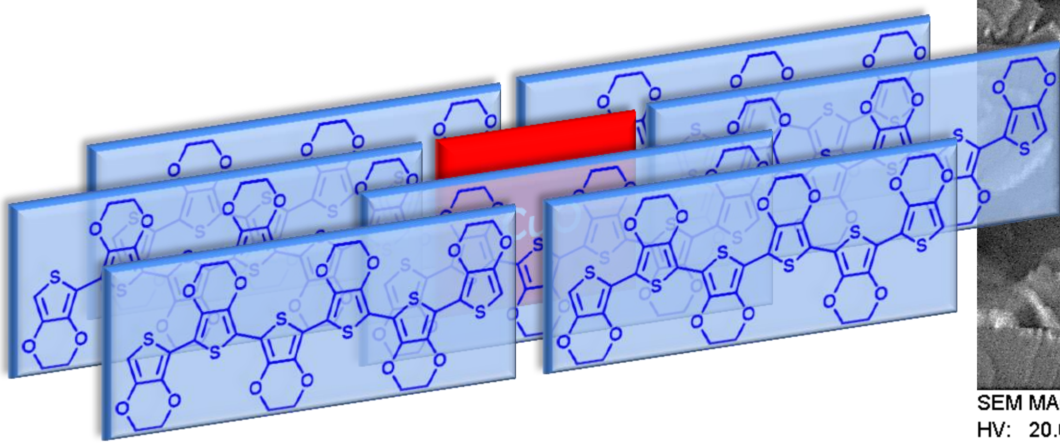
	Chemical Paths	Electrochemical Paths
Polymerization	✓ Easy process ✓ Insulant substrate ✓ Easy to embed nanomaterials ✗ Low control process	✓ Good control process ✗ Conductive substrate ✗ Low thickness films
Doping	✓ No need of conductive substrate ✗ Low control process ✗ Need of properly designed set up	✓ High control level ✓ Standard set up ✗ Need of conductive substrate

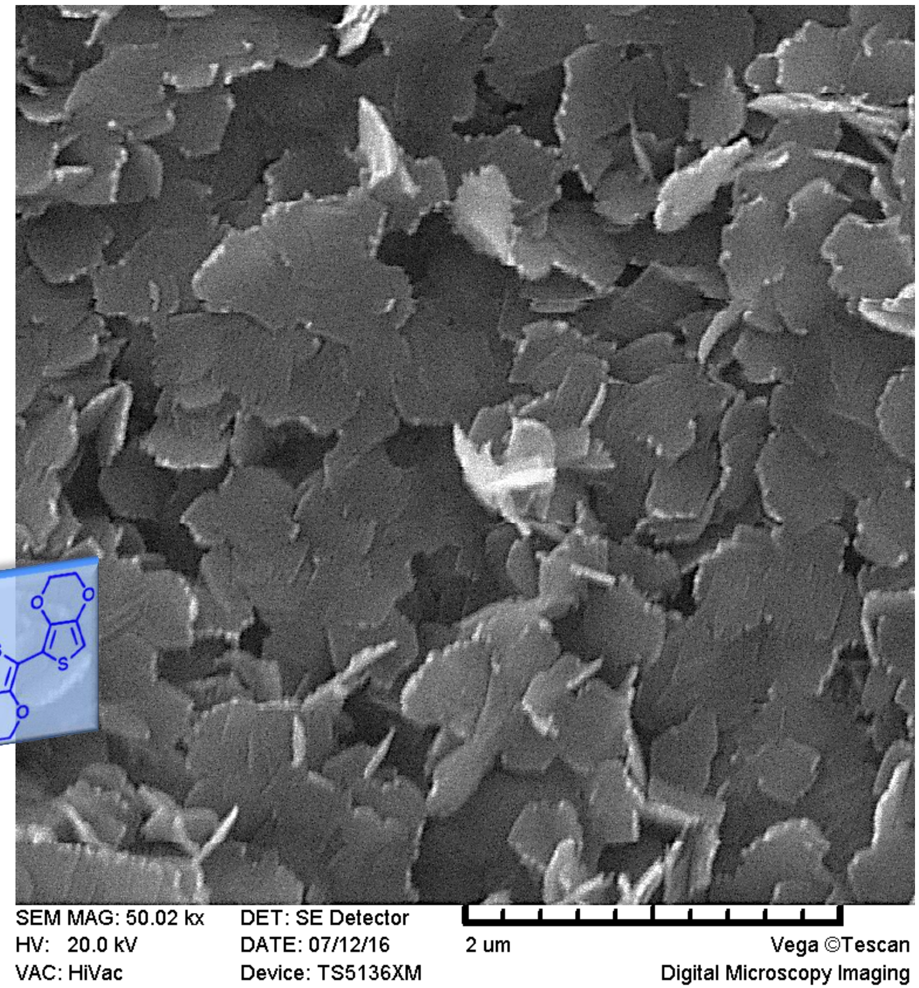
Nanocomposite Film Making: CuO Nanolamellae

CuO

p-type material

work function: 5,3 eV





Y. Li et al. *J. Colloid Interface Sci.*, 2010, **348**, 303–312.

Nanocomposite Film Making: Samples

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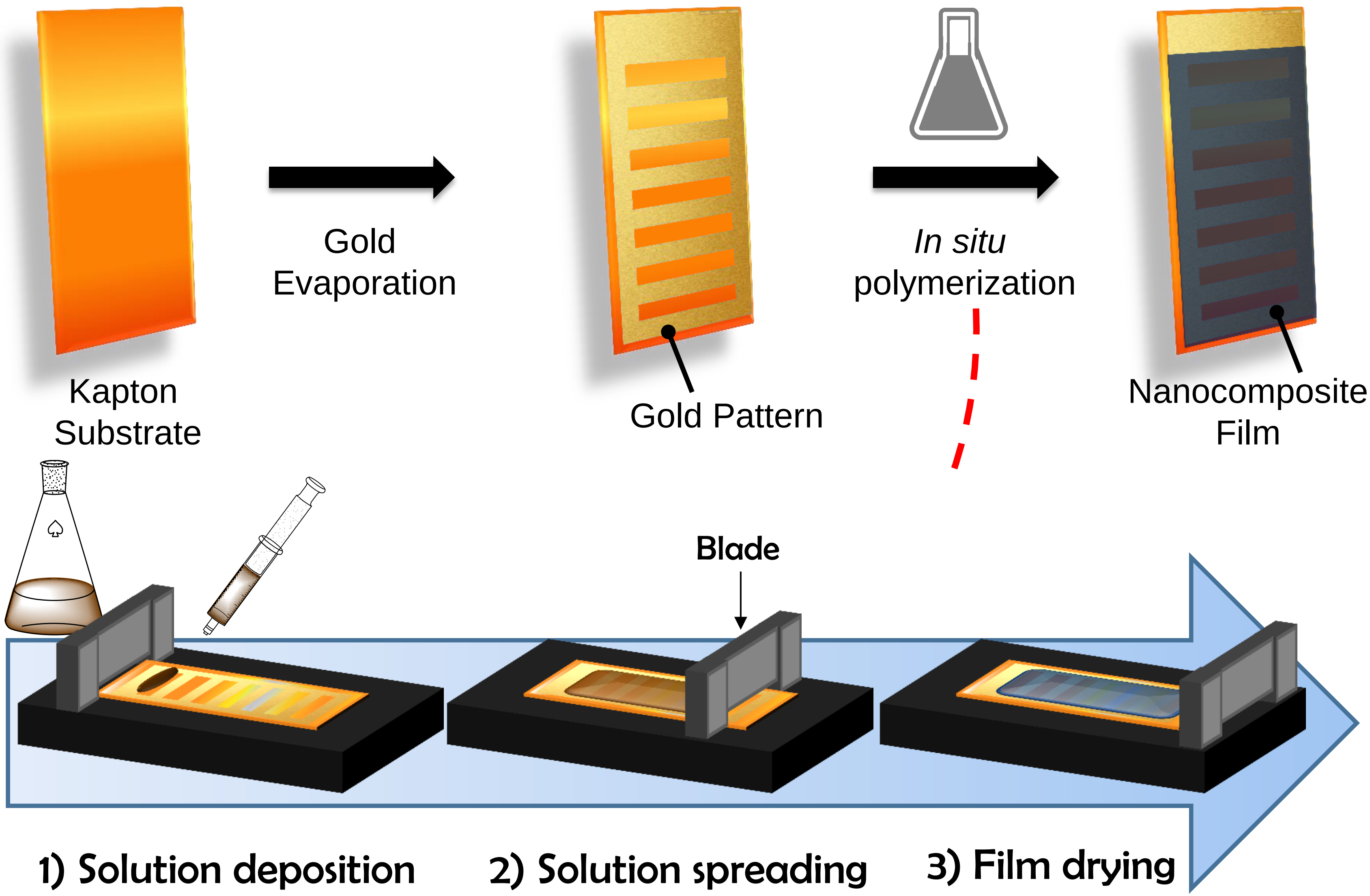

T. Park et al., *Energy Environ. Sci.*, 2013, **6**, 788.

Oxidation Level Tuning

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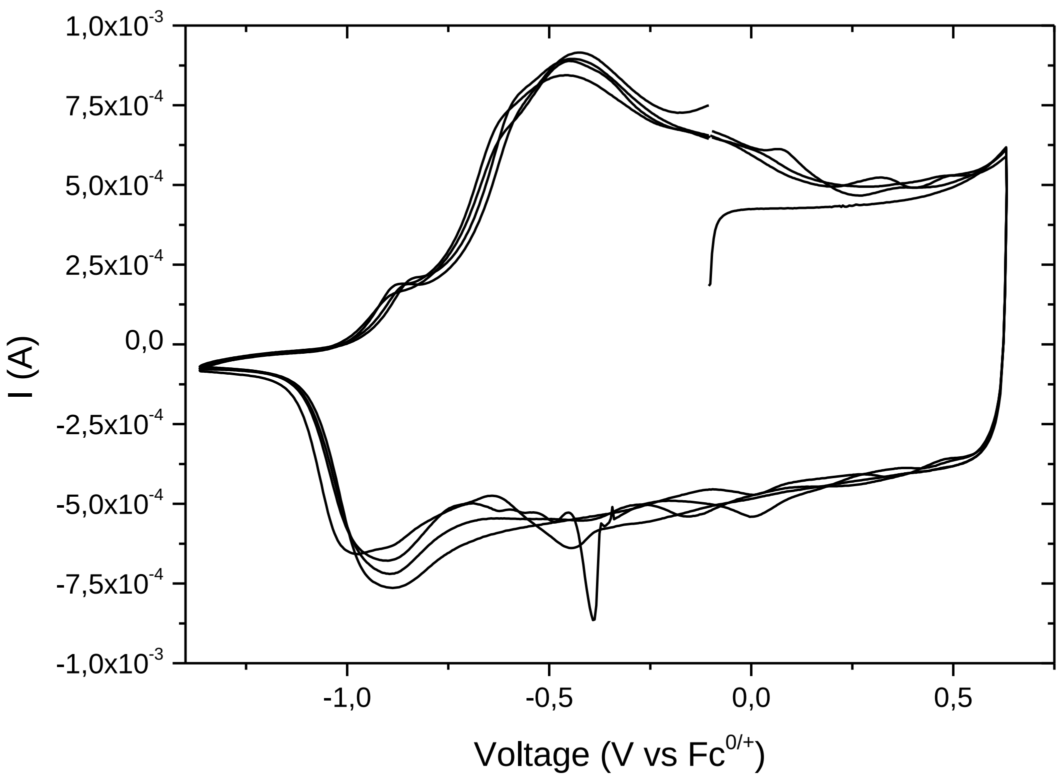

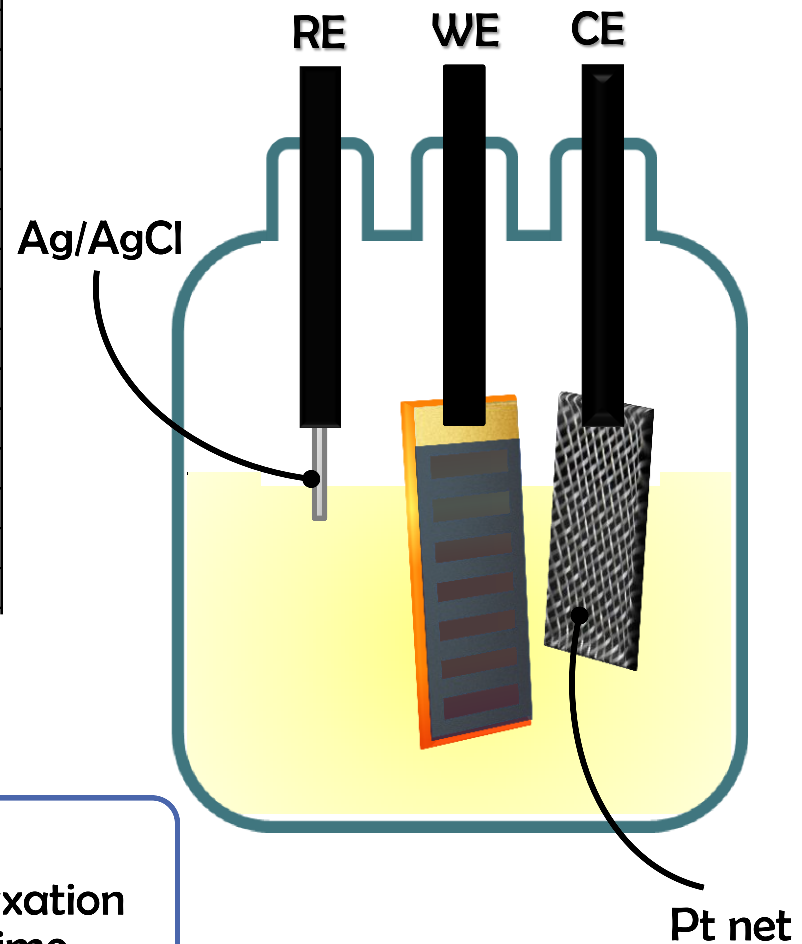

5 cycles of CV (3 mV/s) → Linear Scan to desired potential (1 mV/s) → Relaxation Time

Nanocomposite Film Making: Samples

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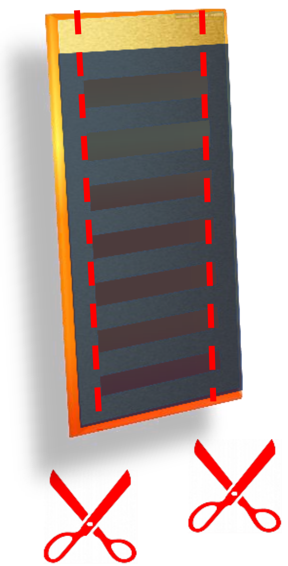
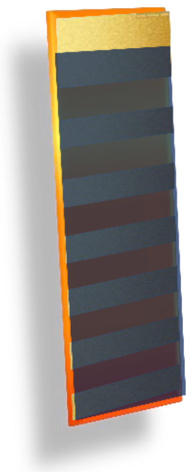
Continuous gold pattern
Not measurable sample

Discontinuous gold pattern
Measurable sample



Cutting



Thermoelectric Measurements

Modified Oxidation Level Sample

Charge Transport Properties

Charge Transport model for conducting polymers

Stephen Dongmin Kang[1] and G. Jeffrey Snyder[2] (Private communication)

[1]Department of Applied Physics and Material Science, California Institute of Technology, CA 91125, USA
[2]Department of Materials Science and Engineering, Northwestern University, IL 60208, USA

Parameters

$\sigma_{E_0}(T)$ transport coefficient

s transport parameter

$$\eta = \frac{E_F - E_t}{k_B T} \ll -1$$

non-degenerate limit

$(E_t: transport\ edge)$

Transport function: $\sigma_E(E,T) = \sigma_{E_0}(T) \cdot \left(\frac{E - E_t}{k_B T}\right)^{s} \quad E > E_t$

$= 0 \quad E < E_t$

Electrical conductivity: $\sigma = \int \sigma_E \left(-\frac{\partial f}{\partial E}\right) dE$

$$\sigma = \sigma_{E_0}(T)\, s\, \Gamma(s)\, e^{\eta}$$

Seebeck Coefficient:

$$S = \frac{1}{\sigma}\left(\frac{k_B}{e}\right)\int \left(\frac{E - E_t}{k_B T}\right)\sigma_E \left(-\frac{\partial f}{\partial E}\right) dE$$

$$S = \frac{k_B}{e}\left[s + 1 - \ln\left(\frac{\sigma}{\sigma_{E_0}\, s\, \Gamma(s)}\right)\right]$$

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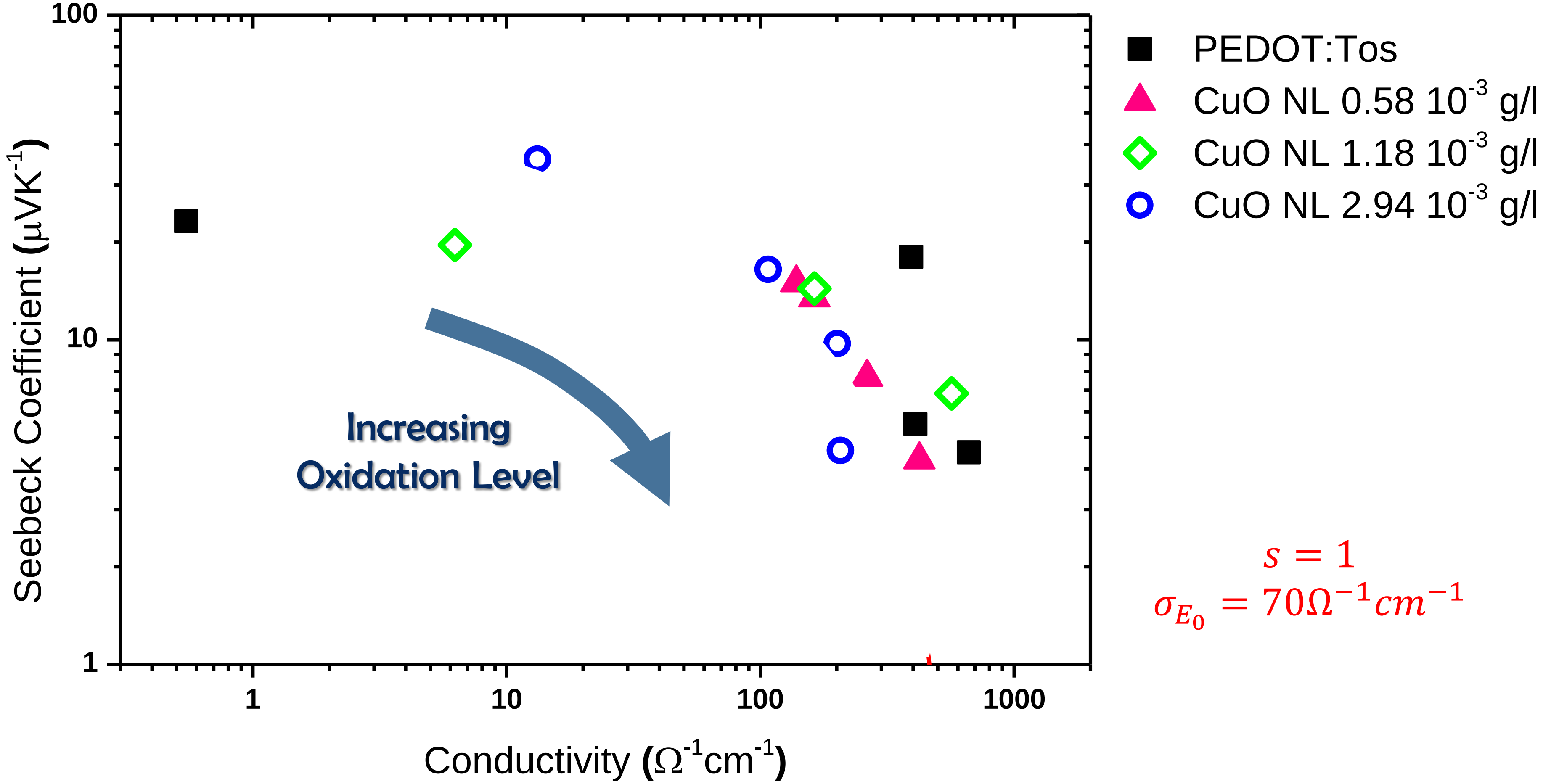
Preliminary Results

$$S = \frac{k_B}{e}\left[s + 1 - ln\left(\frac{\sigma}{\sigma_{E_0} s\Gamma(s)}\right)\right]$$



$$s = 1$$
$$\sigma_{E_0} = 70\Omega^{-1}cm^{-1}$$

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Conclusions

Chemical Path

- Preparation of PEDOT based nanocomposite

Electrochemical Path

- Modification of sample oxidation level

Thermoelectric measurements

- Study of charge transport properties of novel materials

Preliminary Conclusions and Further Developments

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Further Developments

Chemical Polymerization

Electrochemical Oxidation Tunining

Method

Different CuO NL concentration → Find charge transport model limits

Different inorganic/organic interphase interactions → Understand interaction role

Thank you for your kind attention!

Questions are welcolme!

Aknowledgments

University of Milano-Bicocca

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University of Pavia

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Charge Transport Model

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Charge Transport model for conducting polymers

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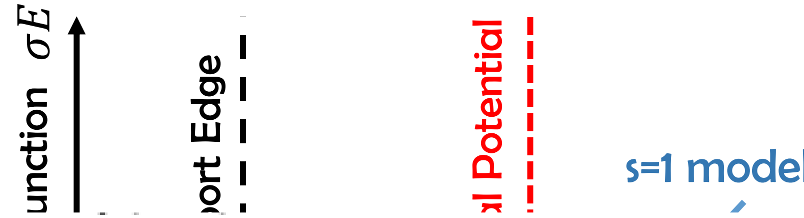
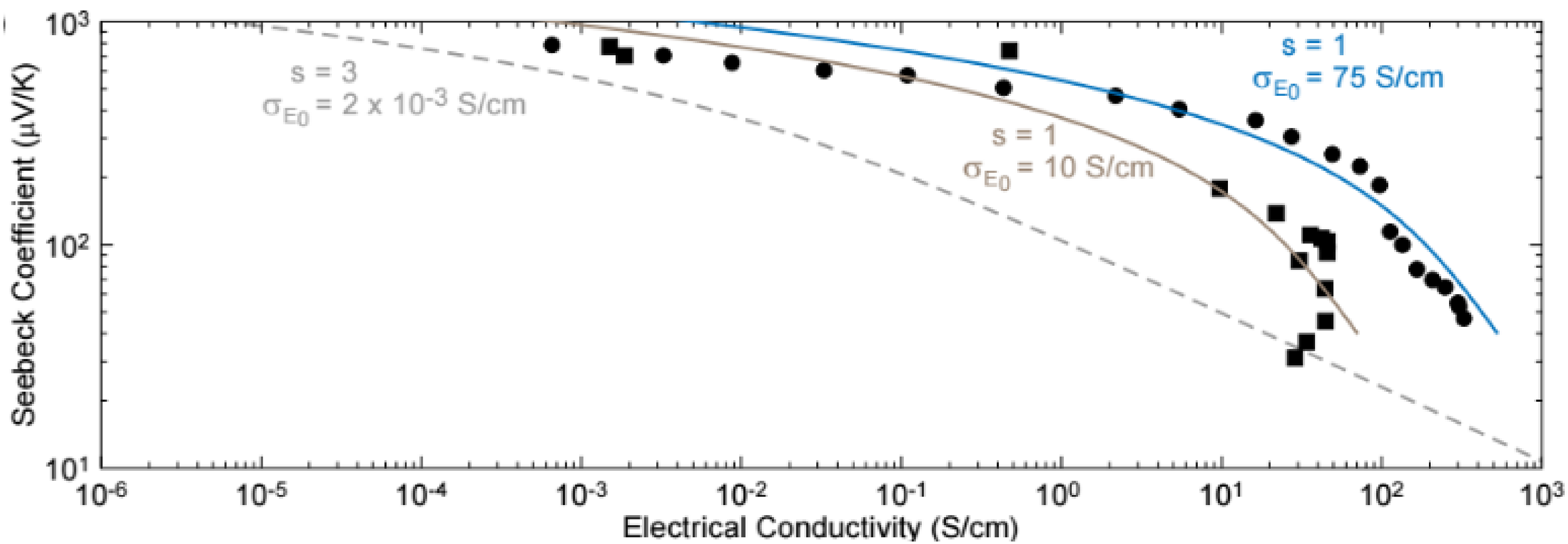
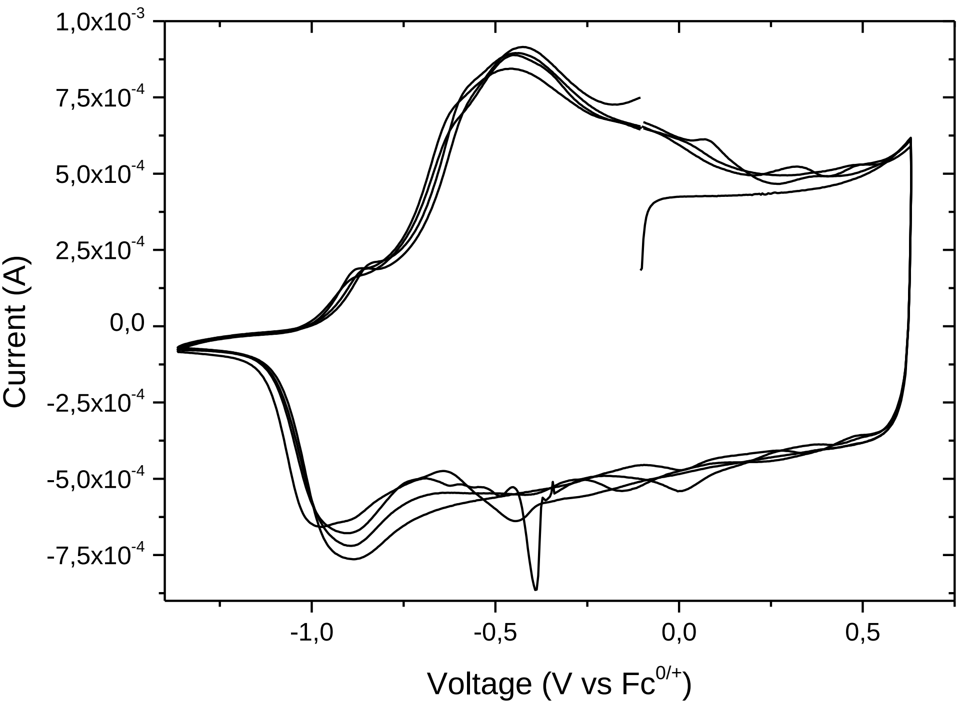
(Private communication)



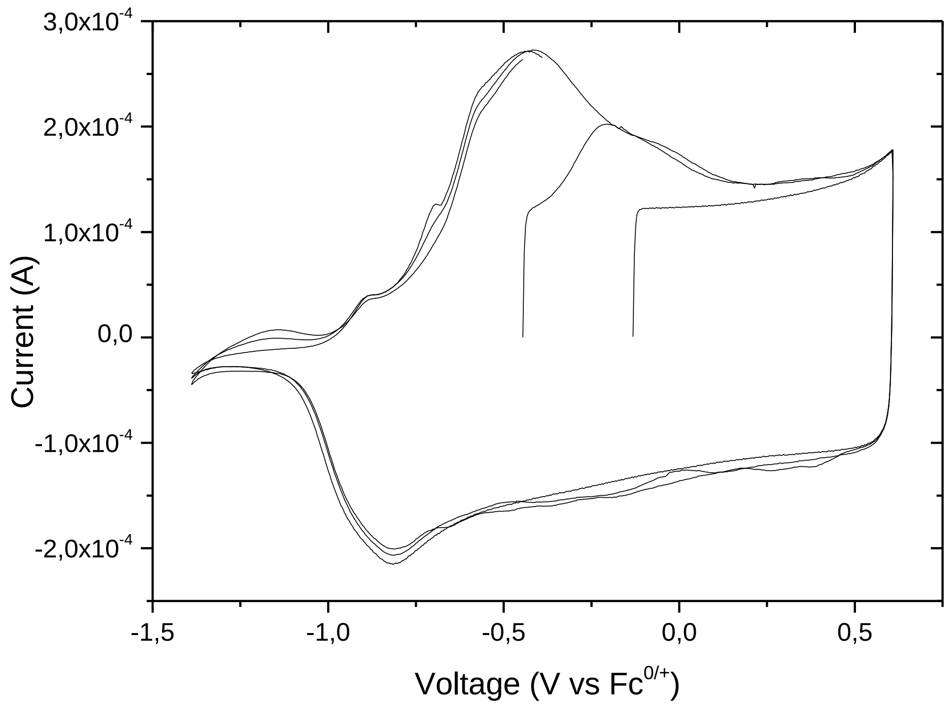


CV Comparison

PEDOT:Tos



PEDOT:Tos/Cu NL $(2.94 \times 10^{-3} g/l)$



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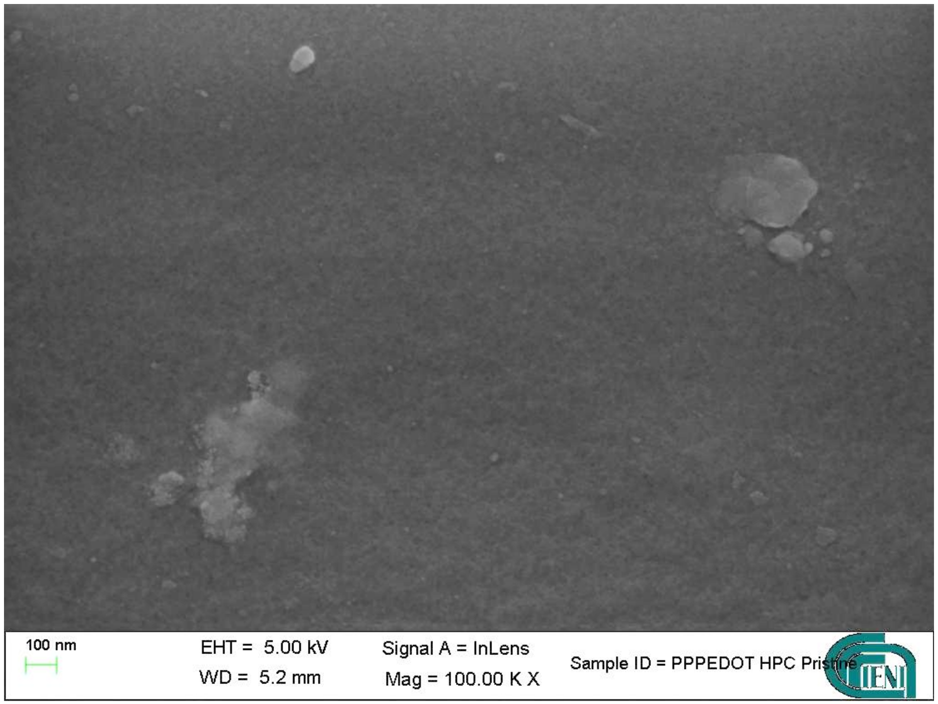
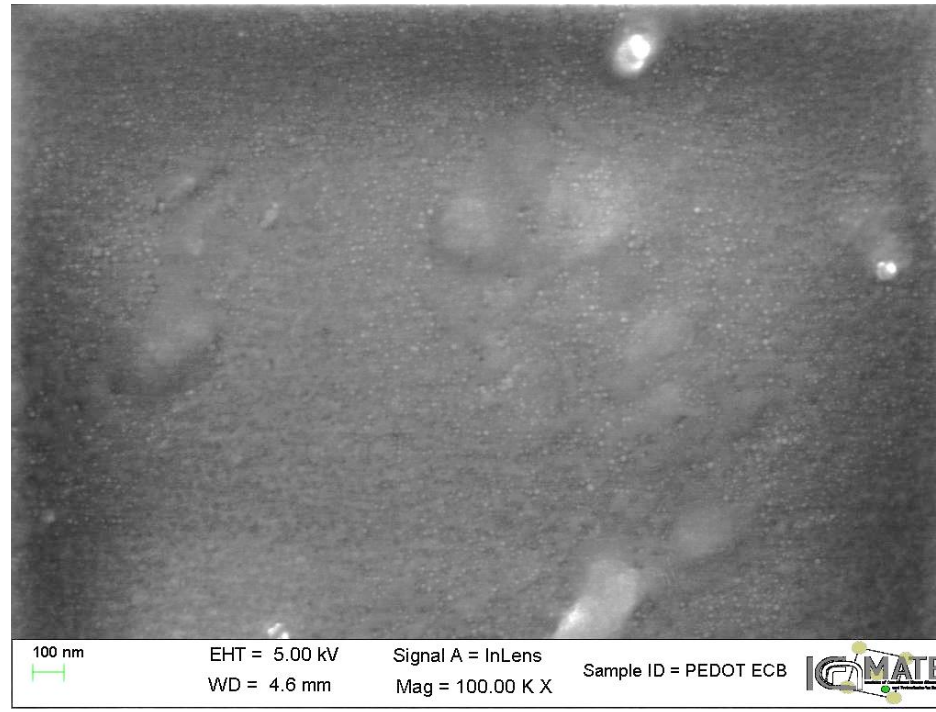
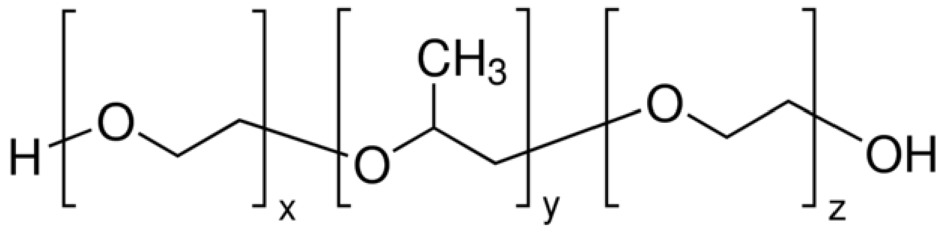
SEM images comparison

PEDOT:Tos before ECT



PEDOT:Tos after ECT





Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol)

Oxidation Level Tuning: Results

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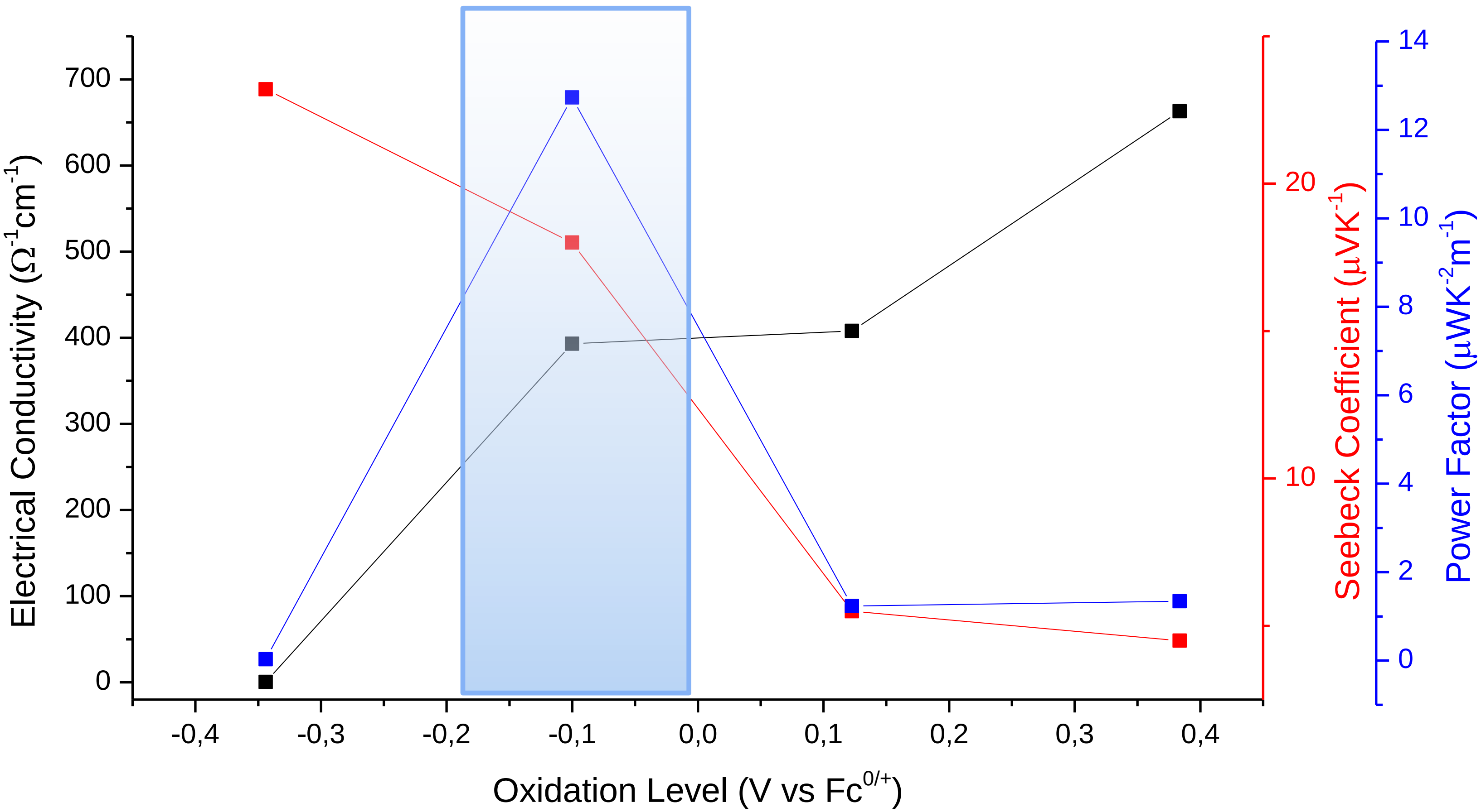
PEDOT:Tos

Optimal oxidation level



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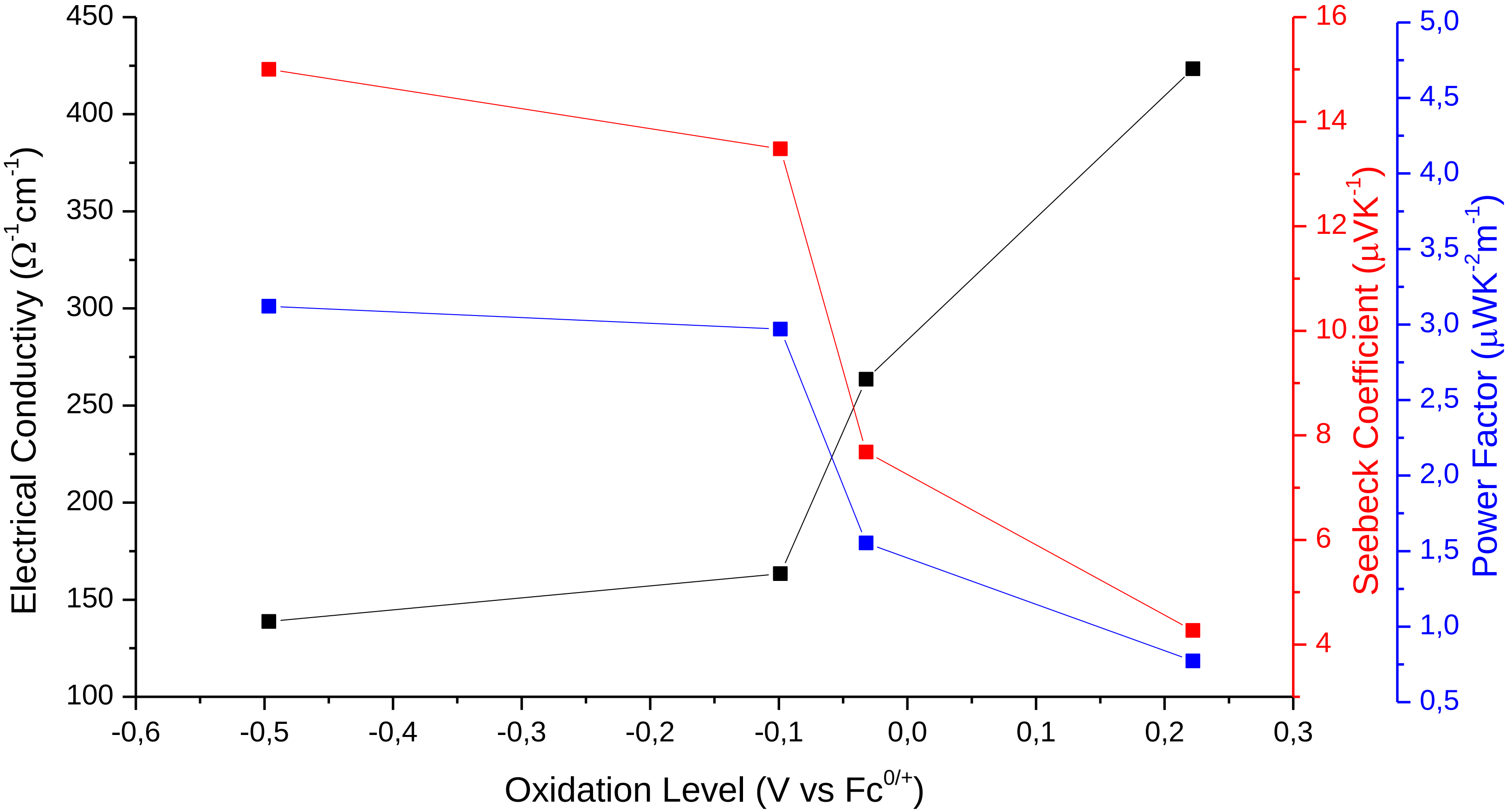
PEDOT:Tos/Cu NL $(0.58 \times 10^{-3} g/l)$



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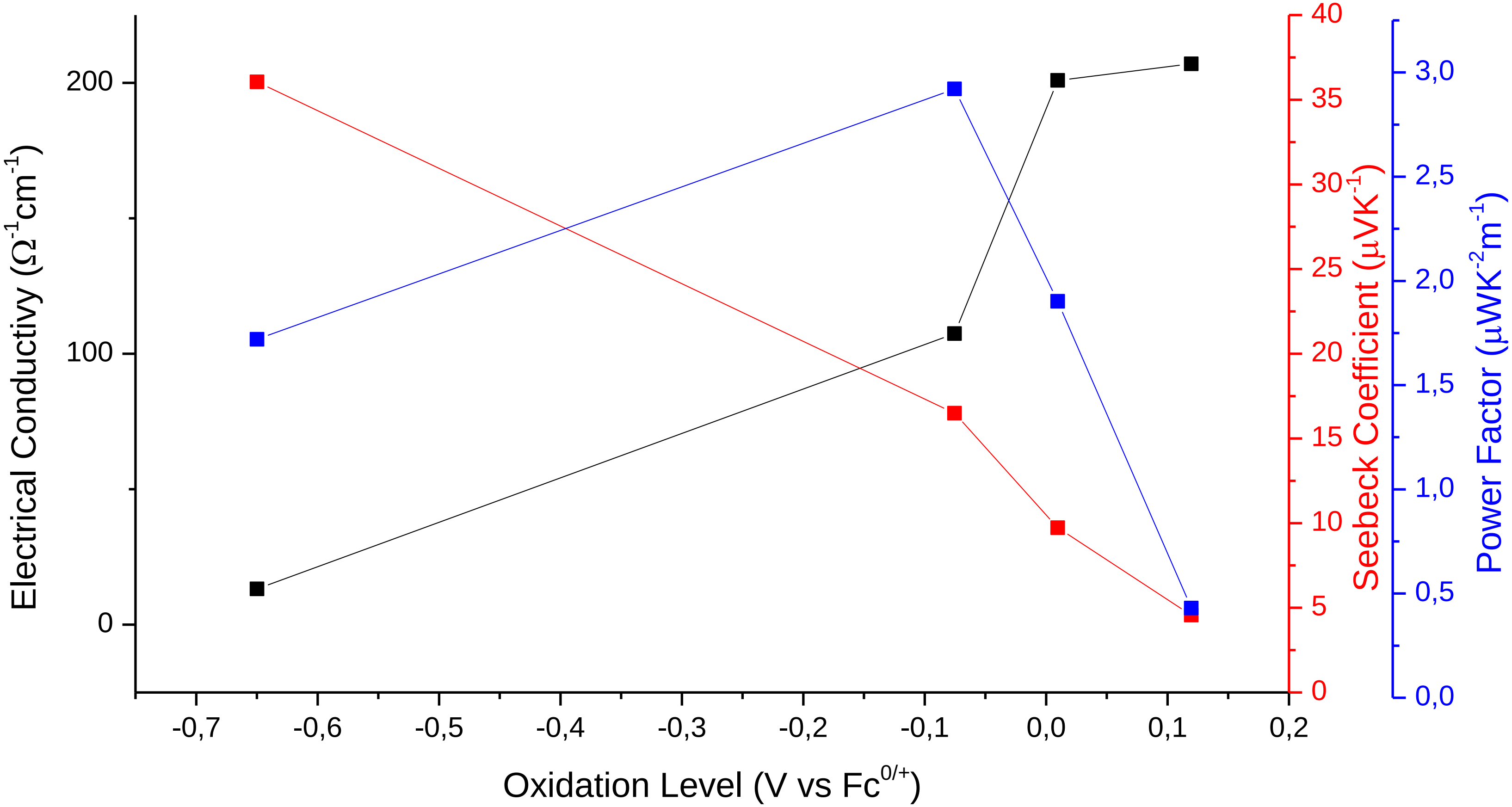
PEDOT:Tos/Cu NL $(2.94 \times 10^{-3} g/l)$



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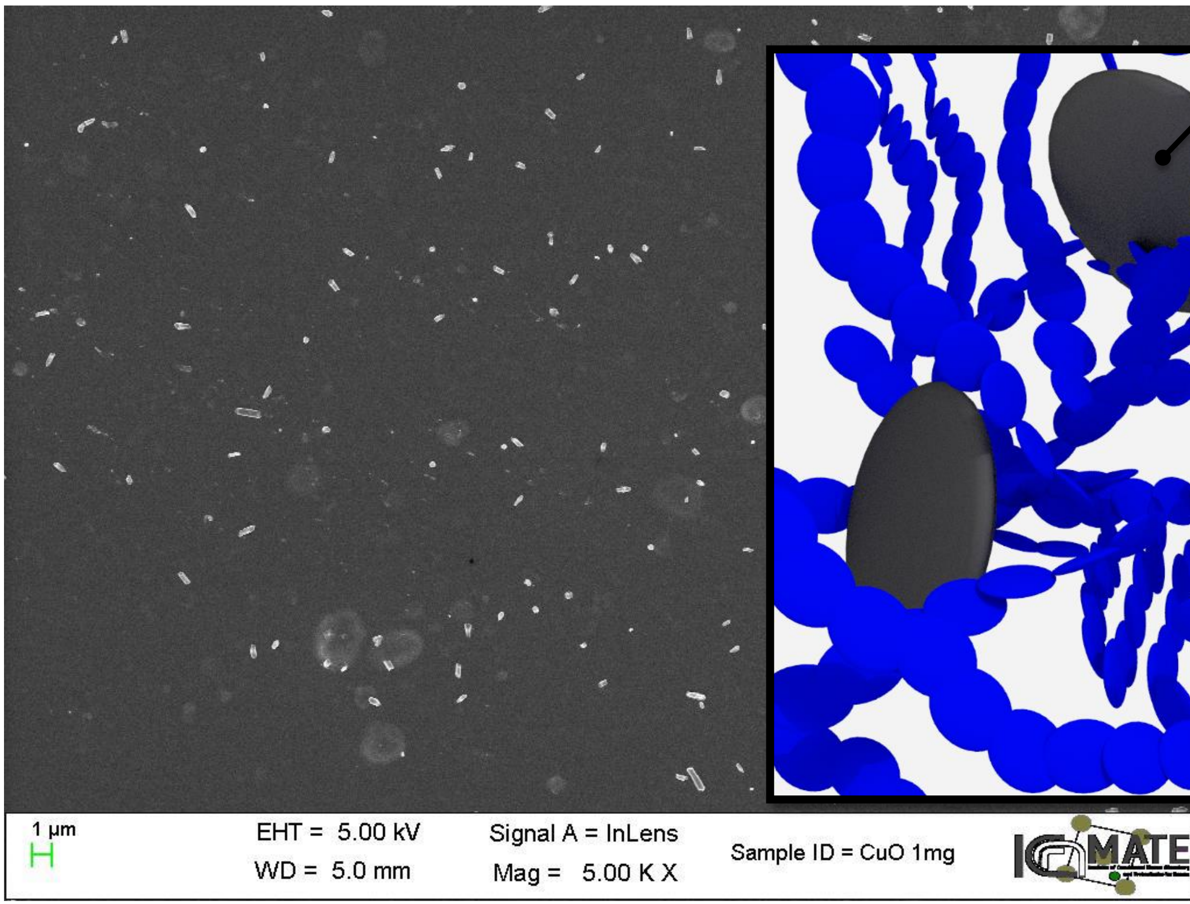
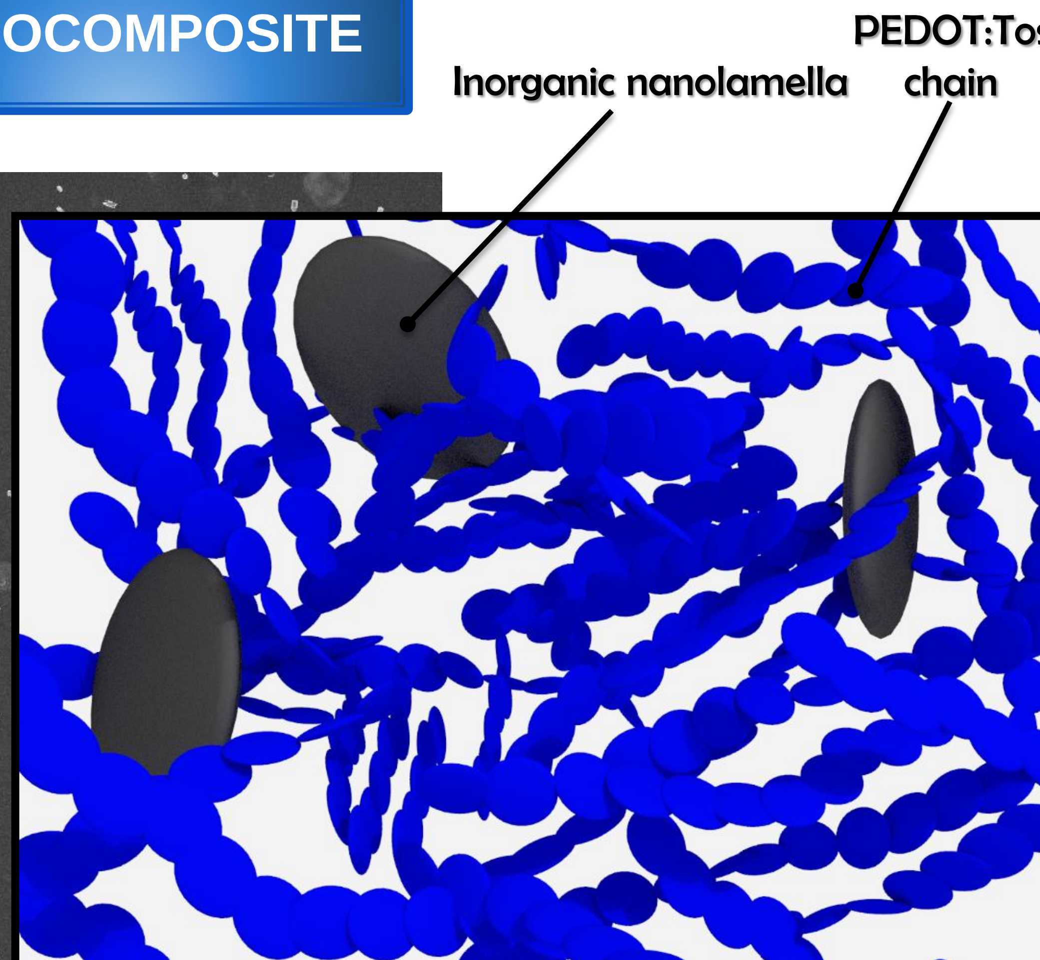
NANOCOMPOSITE





Nanostructuration: Energy Filtering

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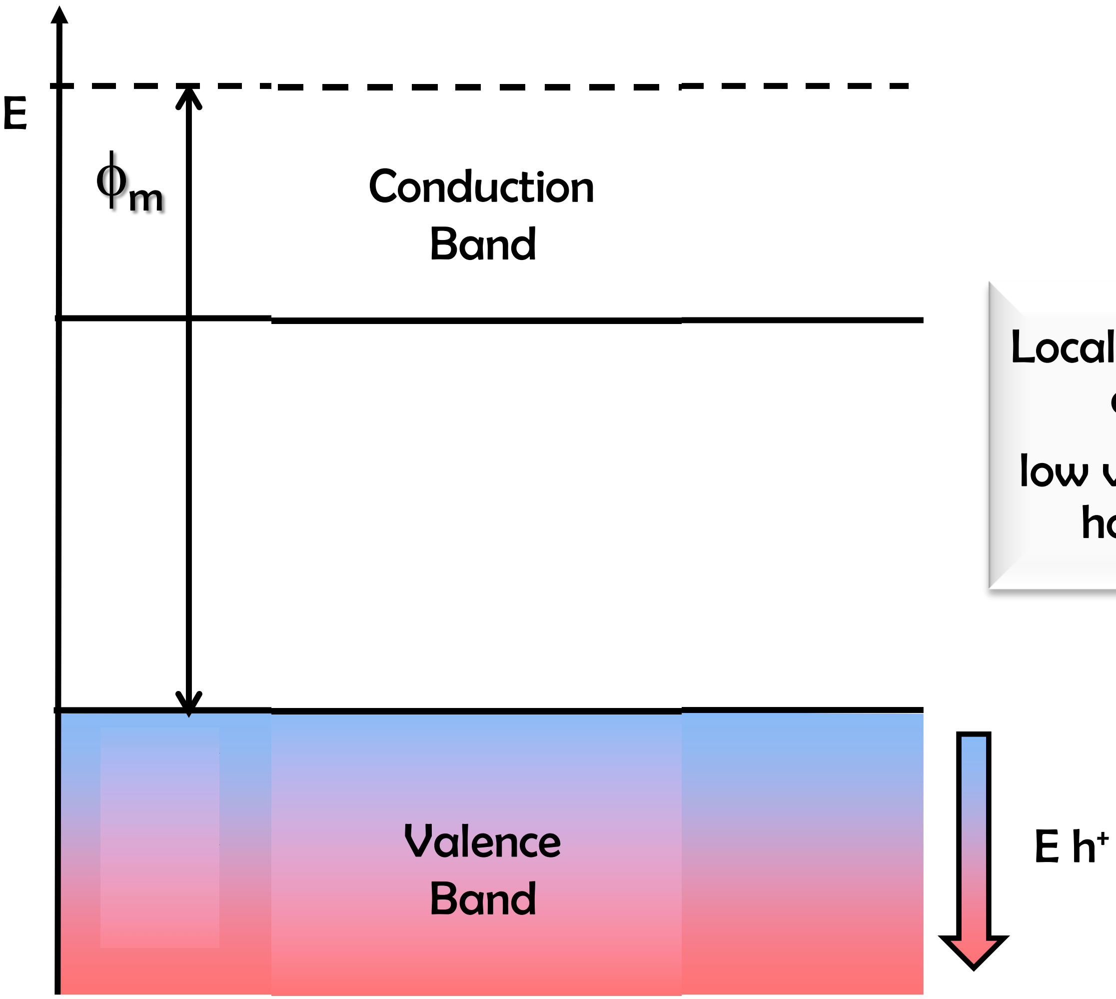

Localization of low velocity holes

- Decrease of carrier concentration *n*
- Increase of average carrier mobility μ

Aim of the work

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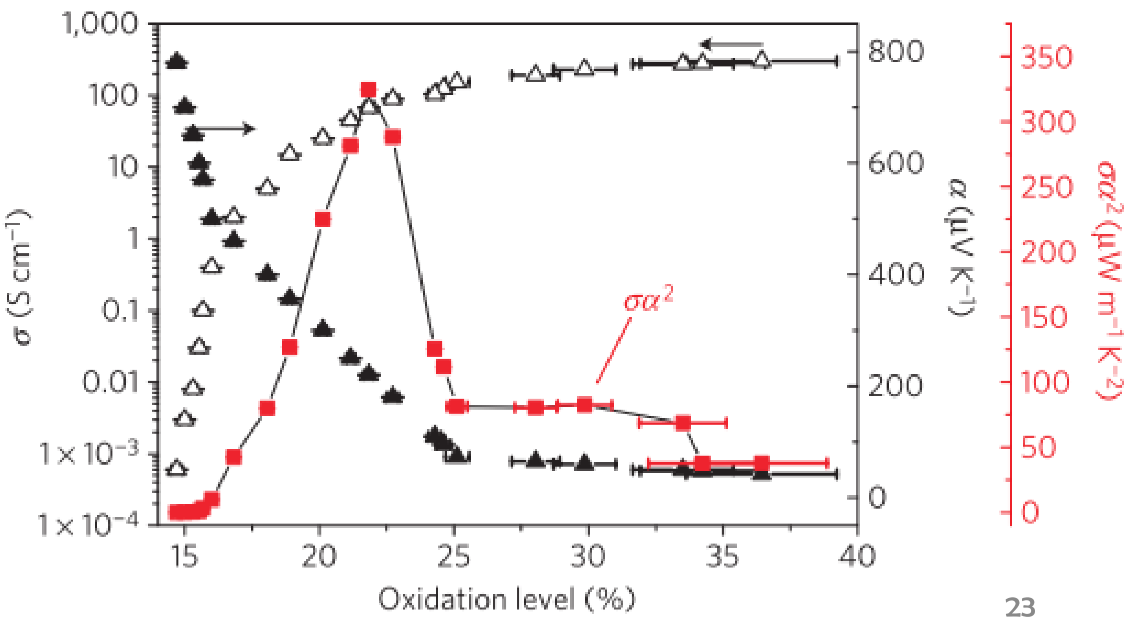
NANOCOMPOSITE

Materials	S (μV/K)	PF (μW/m K^2)	*ZT*
PEDOT:PSS/SWCNT	30	25	0.02
PEDOT:PSS/MWCNT	70	500	-
PEDOT:PSS/Bi_2Te_3	60	130	0.1
PEDOT:PSS/Te	163	70.9	0.1
PEDOT:PSS/Au NPs	26.5	51.2	~0.1
PEDOT:PSS/Au nanorods	12	30	-
PEDOT:PSS/Ge	~50	165	0.1

Q. Wei et al. *Materials (Basel).*, 2015, **8**, 732–750.

OXIDATION LEVEL TUNING



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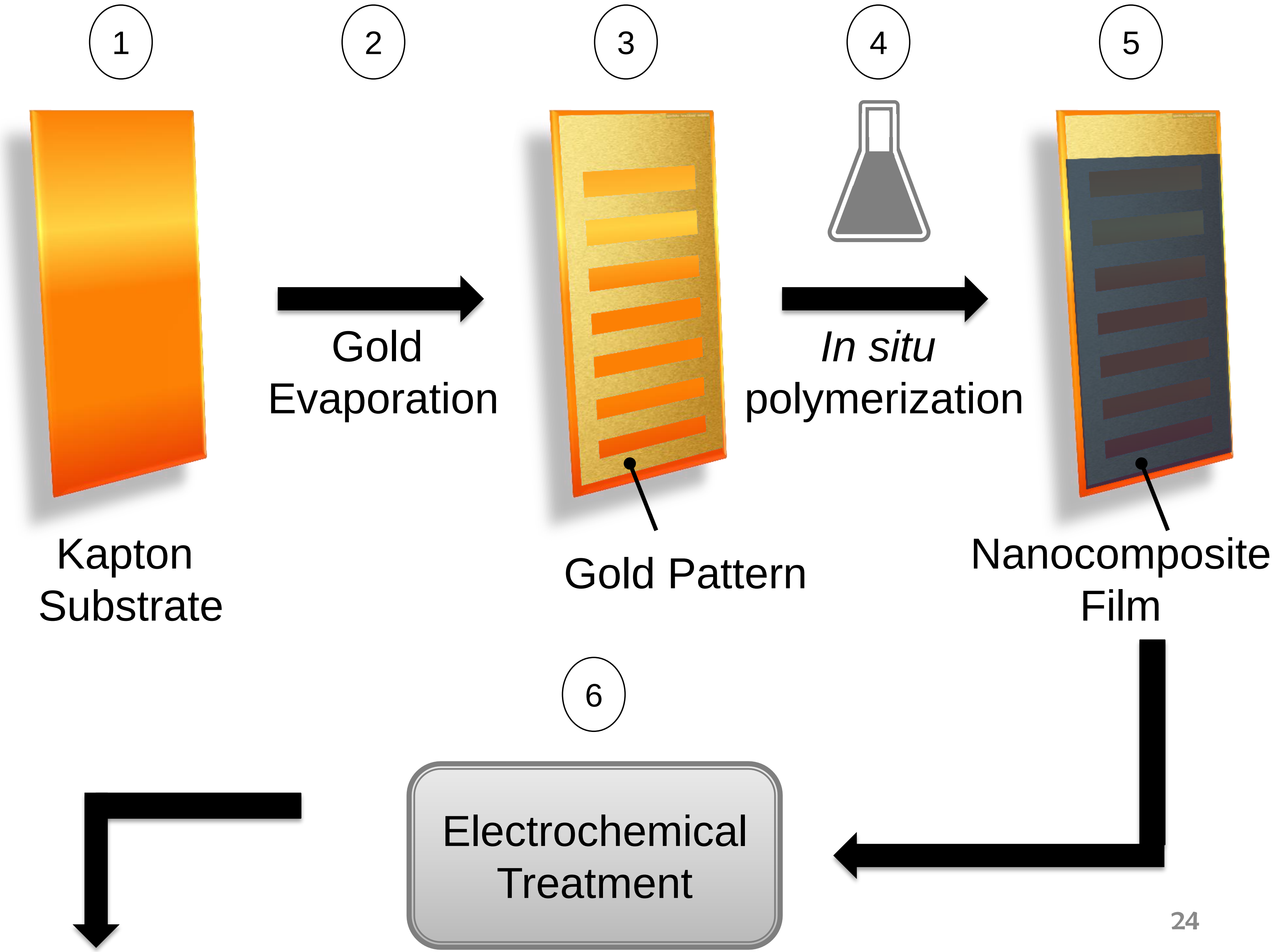
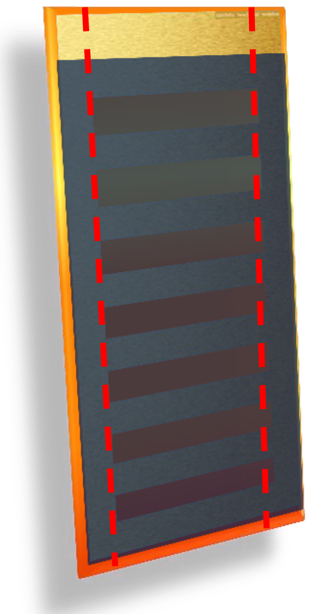

1
2
3
4
5
Gold Evaporation
In situ polymerization
Kapton Substrate
Gold Pattern
Nanocomposite Film
6
Electrochemical Treatment

7

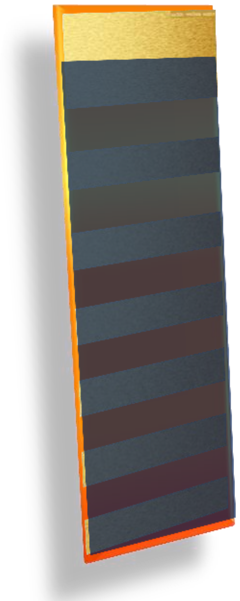


Modified Oxidation Level Sample

8

Cutting

9



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Thermoelectric Measurements