E-MRS European Materials Research Society

Spring Meeting 2016

UNIVERSITÀ DEGLI STUDI DI MILANO BICOCCA

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Conjugated Polymer Nanocomposite

Towards a Novel Material for Thermal Energy Microharversting

Introduction

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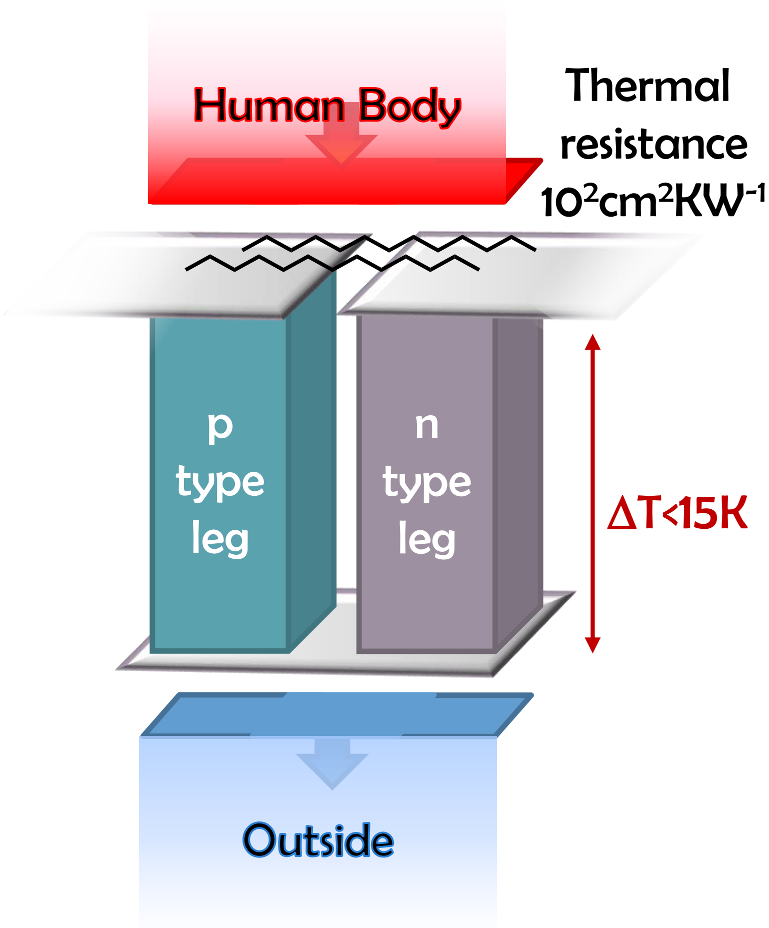
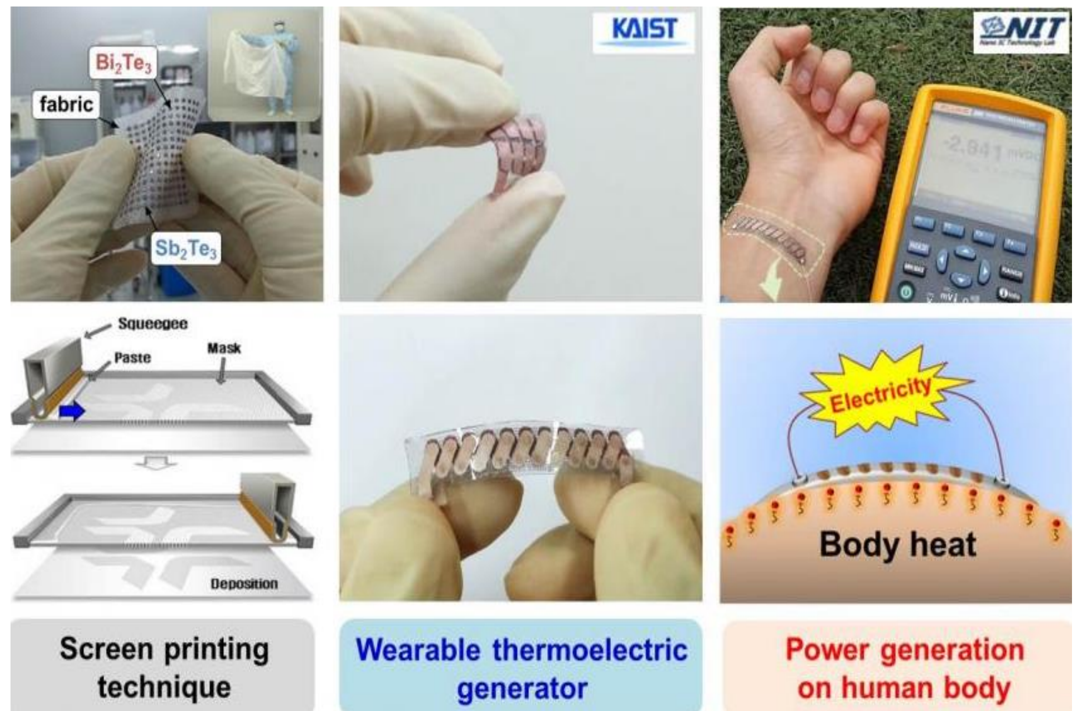
Wearable Thermoelectric Microharvesters





Power Density
$3{,}82\ \mu W/cm^2$

Kim, S. J., We, J. H. & Cho, B. J. A. *Energy Environ. Sci.* **7,** 1959 (2014)

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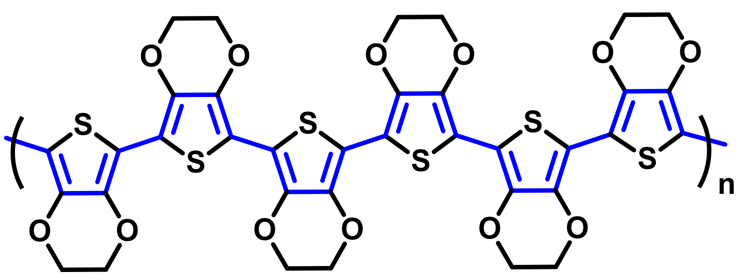
Introduction

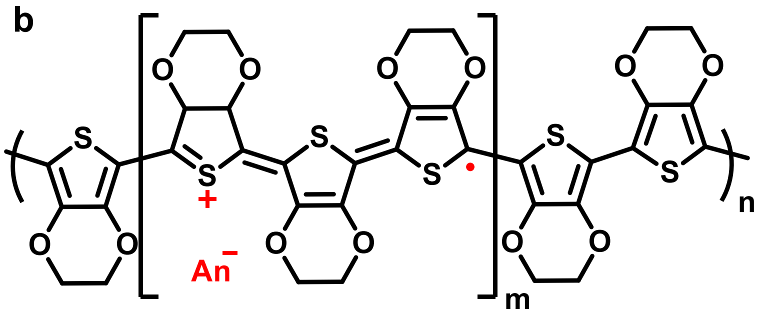
Conjugated Polymers

Poly(3.4-ethylendioxythiophene)
PEDOT

a



b



An^- = Tos^-, Cl^-, PSS^-, ecc

Low TE efficiency

Nanostructuration

Bubnova, O. *et al.* Semi-metallic polymers. *Nat. Mater.* **13**, 190–4 (2014)

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Conjugated Polymer Nanocomposite

Materials	S (μV/K)	PF (μW/m K^2)	*ZT*	Year
PEDOT:PSS/SWCNT	30	25	0.02	2013
PEDOT:PSS/MWCNT	70	500	-	2010
PEDOT:PSS/Bi_2Te_3	60	130	0.1	2010
PEDOT:PSS/Te	163	70.9	0.1	2013
PEDOT:PSS/Au NPs	26.5	51.2	~0.1	2014
PEDOT:PSS/Au nanorods	12	30	-	2014
PEDOT:PSS/Ge	~50	165	0.1	2014

Wide variety of materials!

- Nanomaterial
- Synthesis Method

CHOOSING CRITERIA

Q. Wei, M. Mukaida, K. Kirihara, Y. Naitoh, and T. Ishida, *Materials (Basel)*. 8, 732 (2015).

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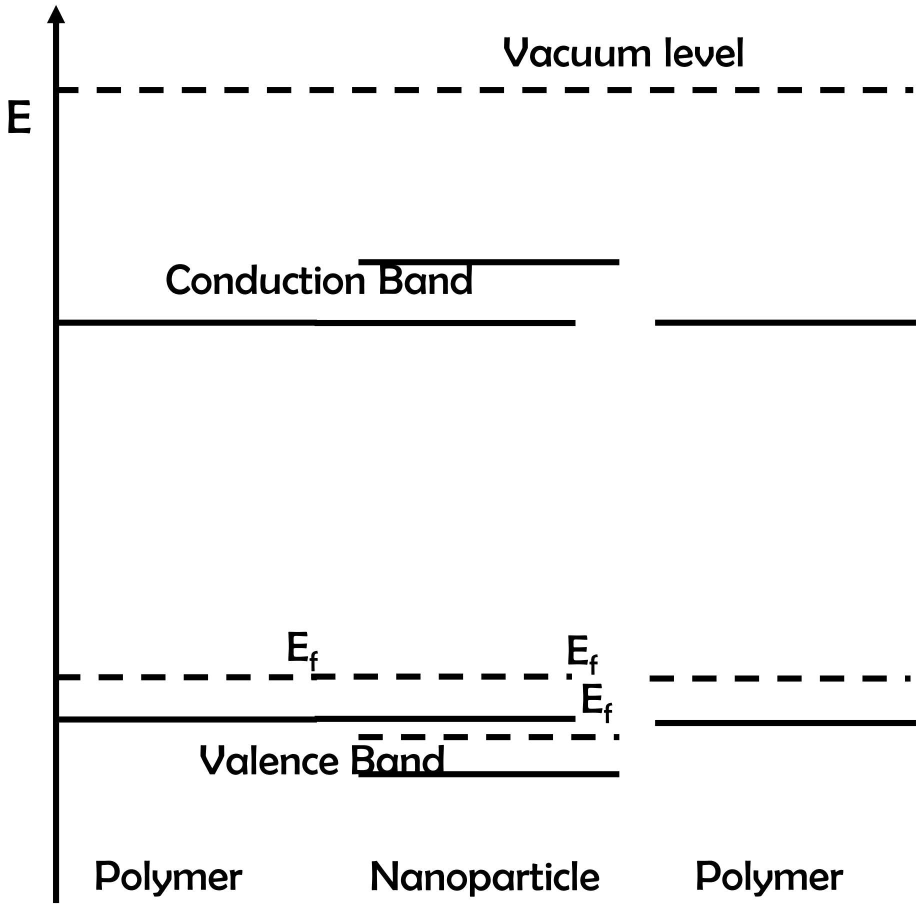
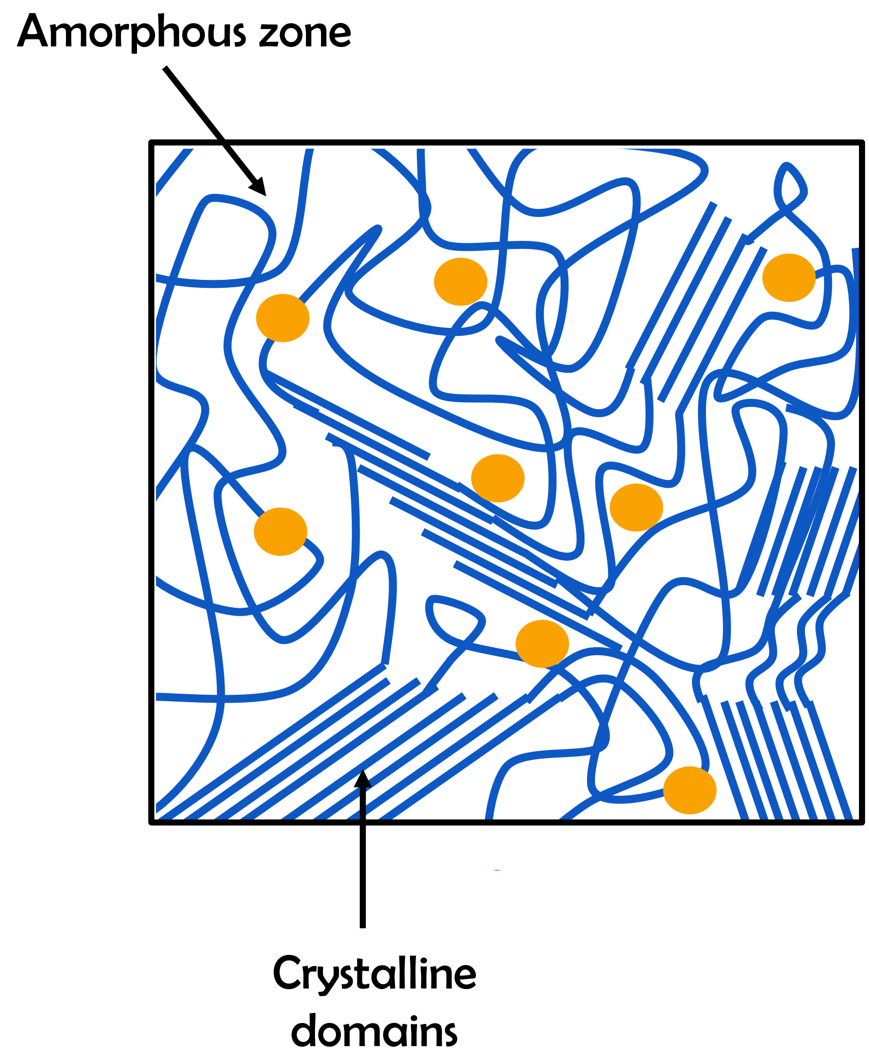
Energy Filtering Effect





N. Neophytou, X. Zianni, H. Kosina, S. Frabboni, B. Lorenzi, and D. Narducci, *Nanotechnology* 24, 205402 (2013).

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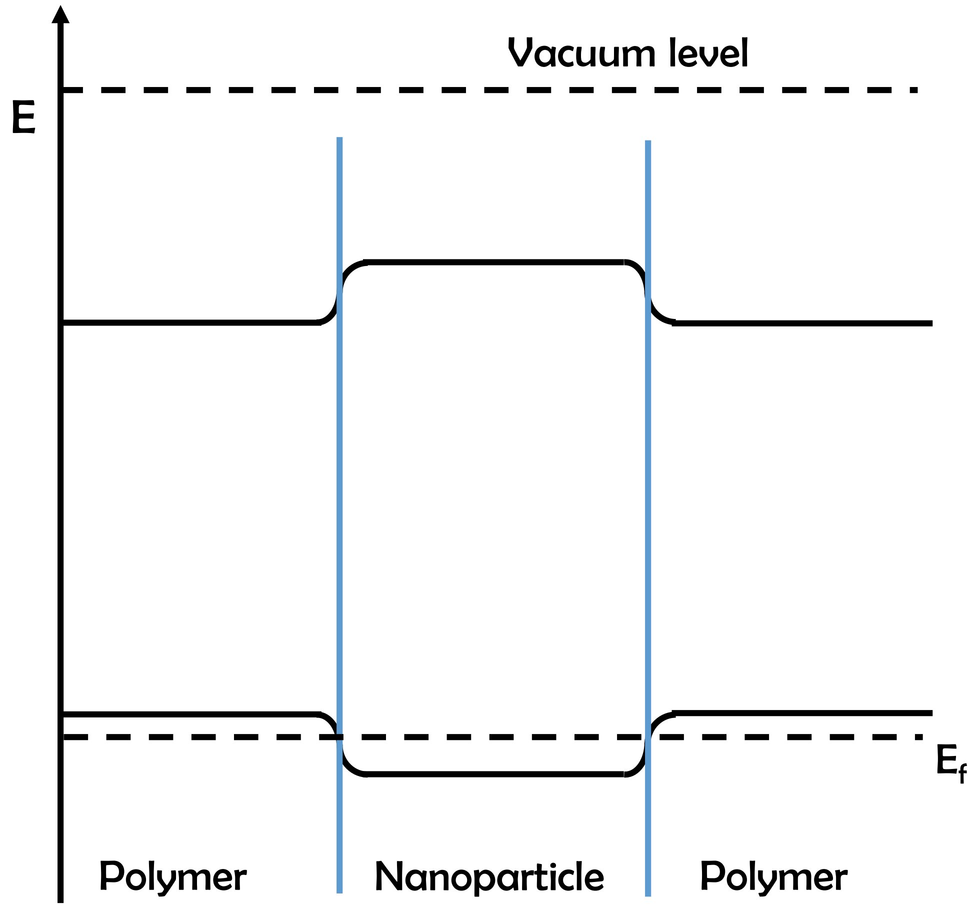
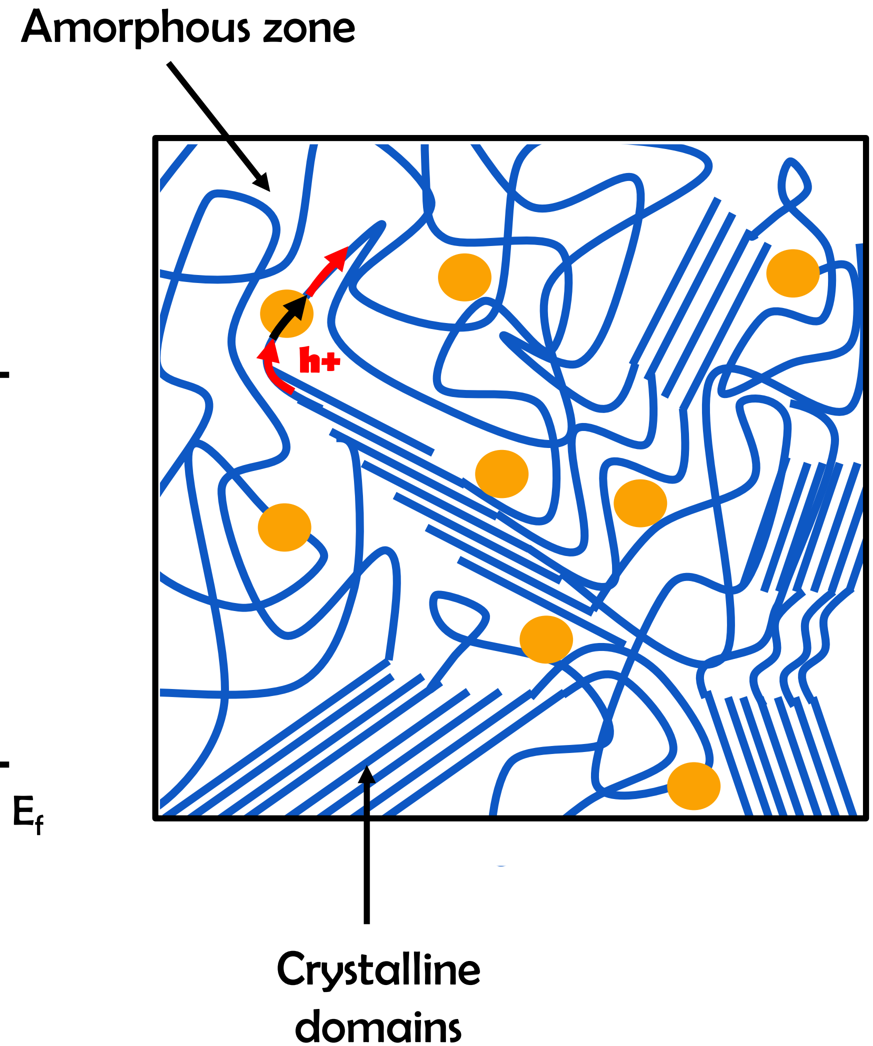
Introduction

Energy Filtering Effect





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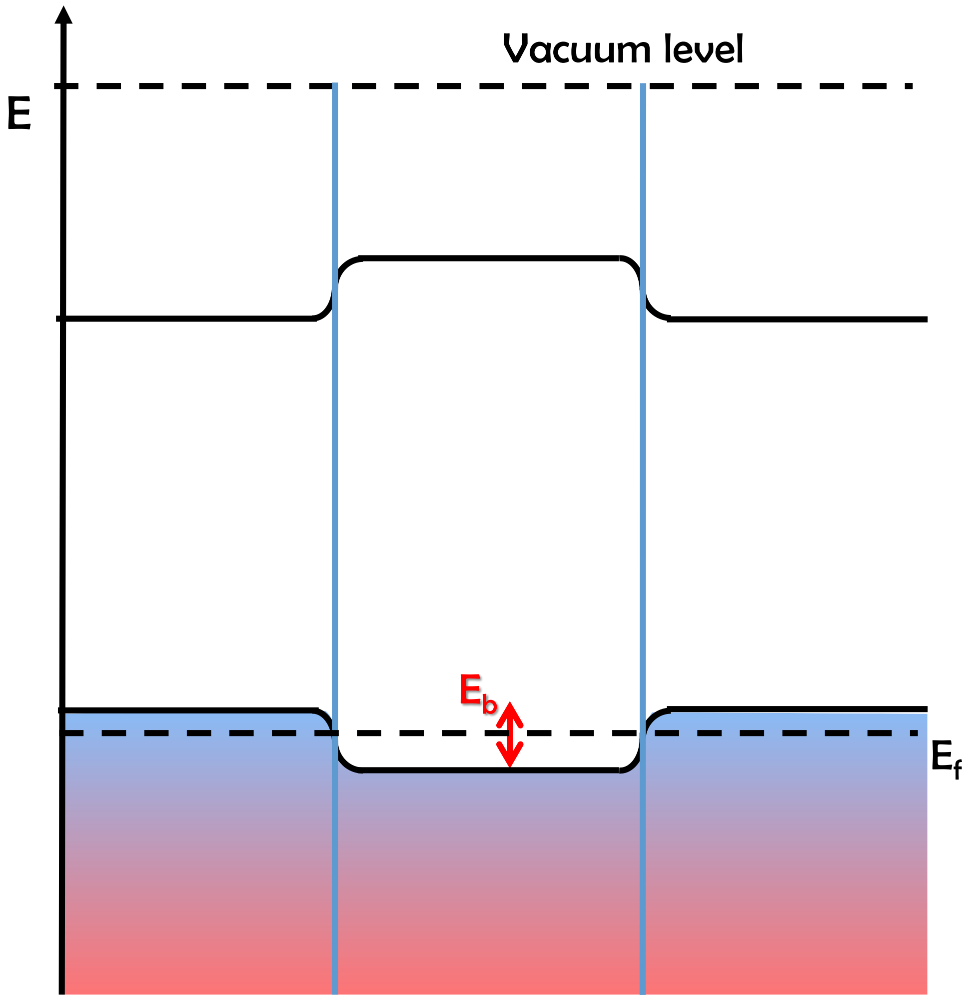
Energy Filtering Effect



$$\alpha = \frac{8\pi^2 k_b^2}{3eh^2} m^* T \left(\frac{\pi}{3\boldsymbol{n}}\right)^{2/3}$$

Localization of low velocity holes

Decrease of carrier concentration

n

Increase of average carrier mobility

μ

$$\sigma = {}^{1}/_{\rho} = \boldsymbol{n} e \mu$$

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Energy Filtering Effect

CHOOSING CRITERIA

- Intimate contacts between CP and NPs

➡ Chemical interaction between CP and NPs

- Similar work functions of the CP and the NPs
- Interfacial barrier height below 100 meV

➡ Choice of CP and NP material

Experimental Work

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Experimental Work

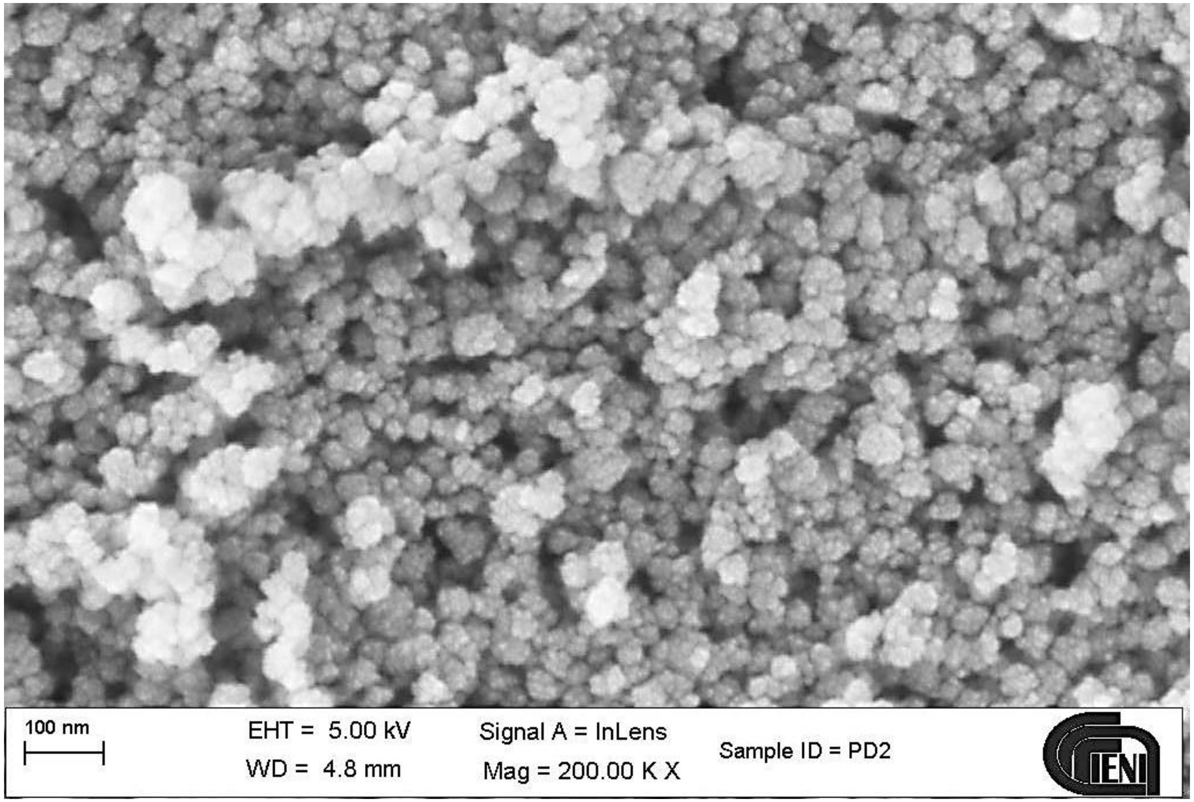
Mn_3O_4 Nanoparticles

Mn_3O_4

p-type material

work function: 4,4 eV

Thanks to Dr. Simone Battiston
IENI-CNR, Padova



Starting salt	Size control agent	Reagent	T (°C)	Size SEM determined (nm)
$MnCl_2 \cdot 4H_2O$	Ethanolamine	H_2O	25	25±6

S. Lei, K. Tang, Z. Fang, and H. Zheng, *Cryst. Growth Des.* 6, 1757 (**2006**)

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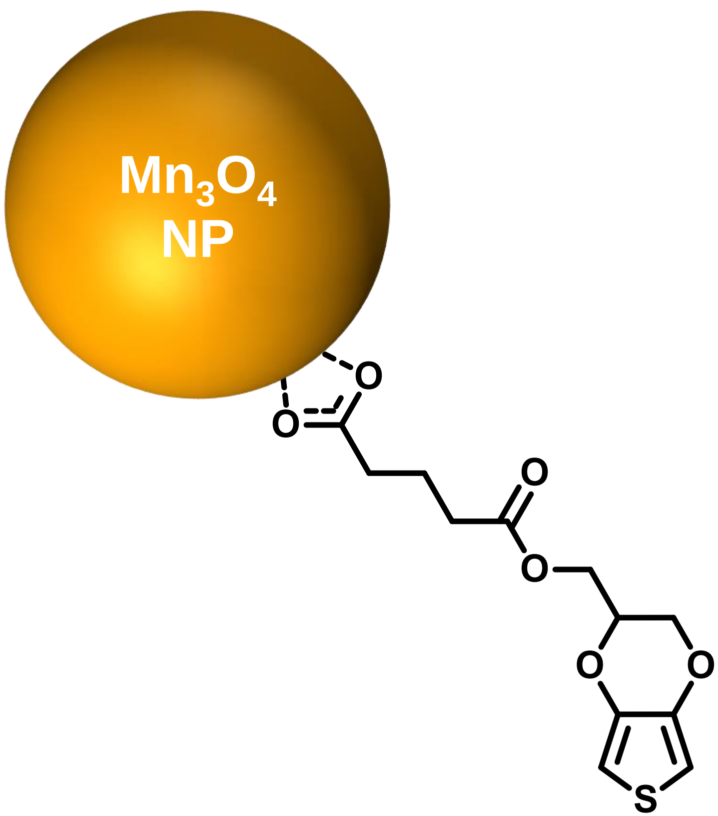
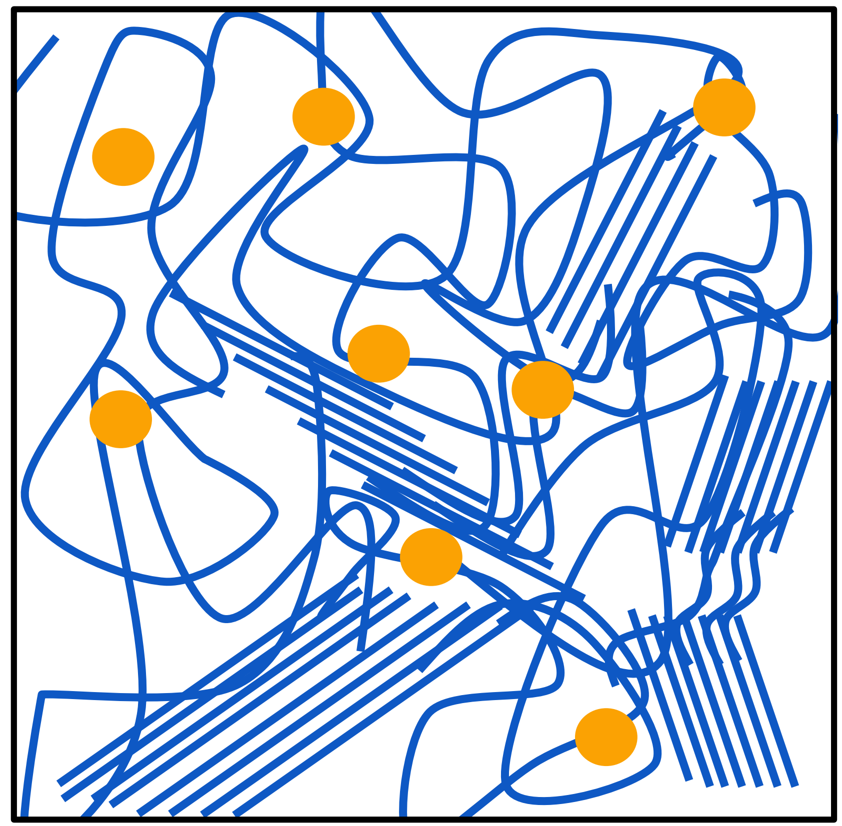
Experimental Work

Nanoparticle Functionalization



Glutaryl-EDOT



✔ Homogeneous dispersion

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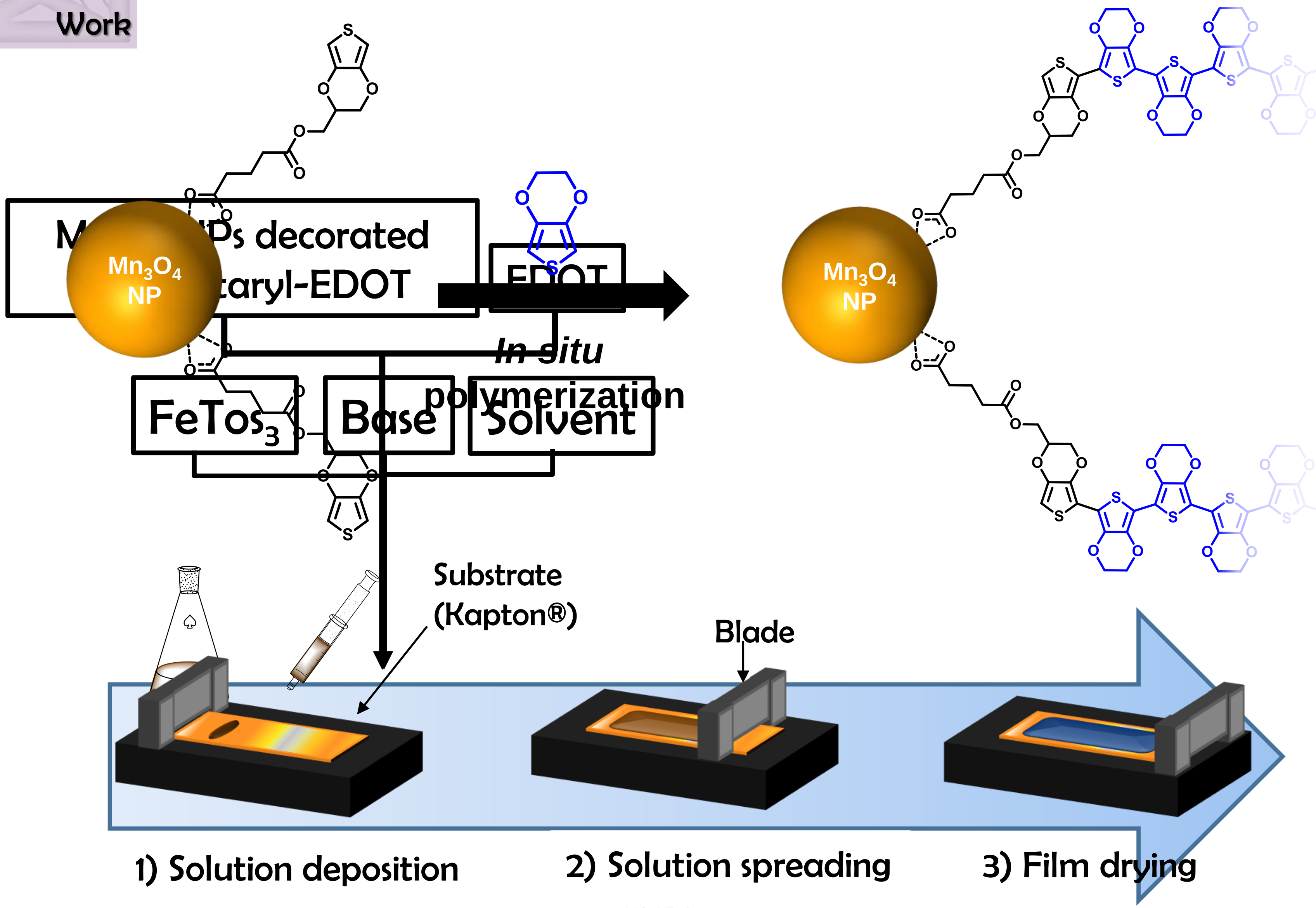
Experimental
Work

Hybrid Film Making



RESULTS

Thermoelectric Characterization

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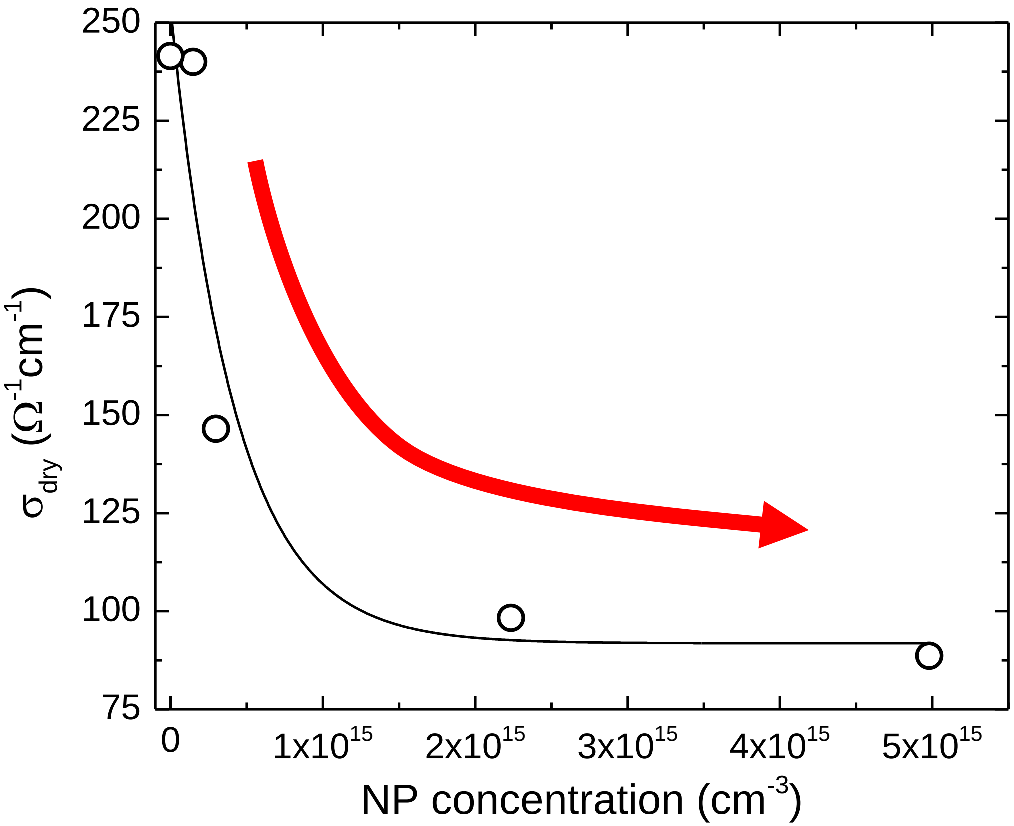
	[NP] (cm^{-3})	σ_{dry} ($\Omega^{-1}cm^{-1}$)	α_{dry} (μVK^{-1})
PEDOT:Tos	0	242±9	15.8±0.9
HF1	$1.5 \cdot 10^{14}$	240±9	14.8±0.5
HF2	$3.0 \cdot 10^{14}$	147±6	15.5±0.7
HF3	$2.2 \cdot 10^{15}$	98±4	15.0±0.2
HF4	$3.0 \cdot 10^{15}$	89±3	15.5±0.8

$$\sigma = ep\mu$$

$$\sigma = ep\left(\mu_0 + \mu_1 e^{-[NP]/N_0}\right)$$



[NP]: NP density
σ: electrical conductivity
α: Seebeck coefficient
e: electronic charge (1.6×10^{-19} C)

p: charge carrier density (holes) [cm^{-3}]
μ: charge carrier mobility [$cm^2/(V \cdot s)$]
μ_0, μ_1, N_0: constants

Results

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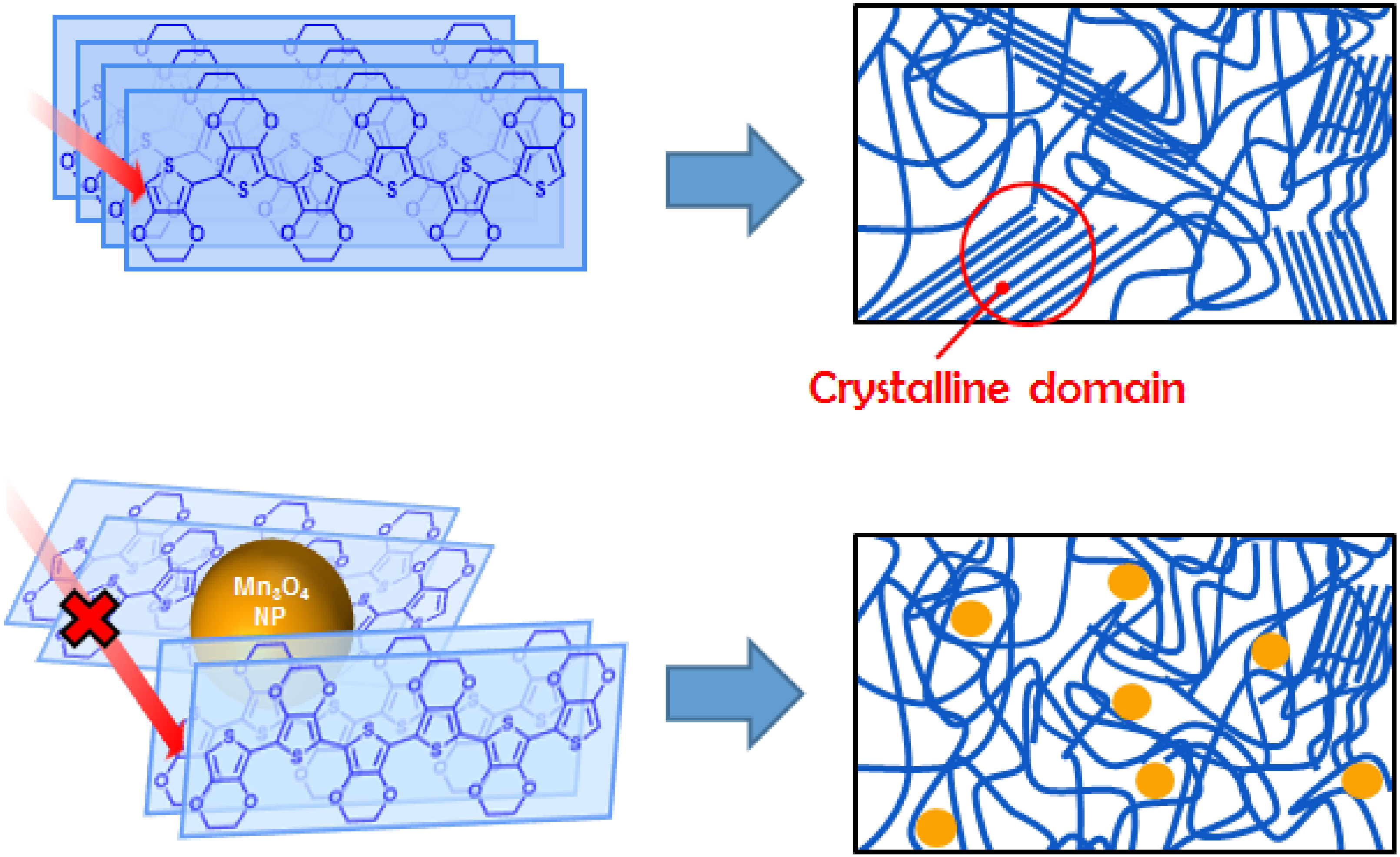
Nanoparticle Influence on Polymer Morphology



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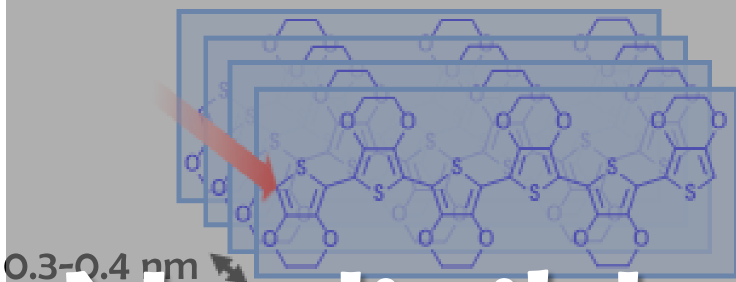
Results

Humidity Effect

Detrimental effect on σ:

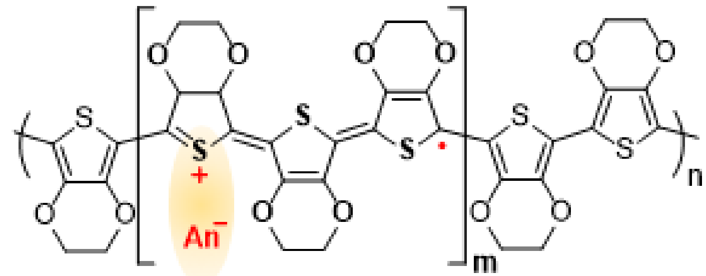
Water interposition between polymer chains



Negligible in NP presence

Beneficial effect on σ:

Counterion solvatation



H. Wang et al., *Adv. Energy Mater.* 5, 1 (2015).

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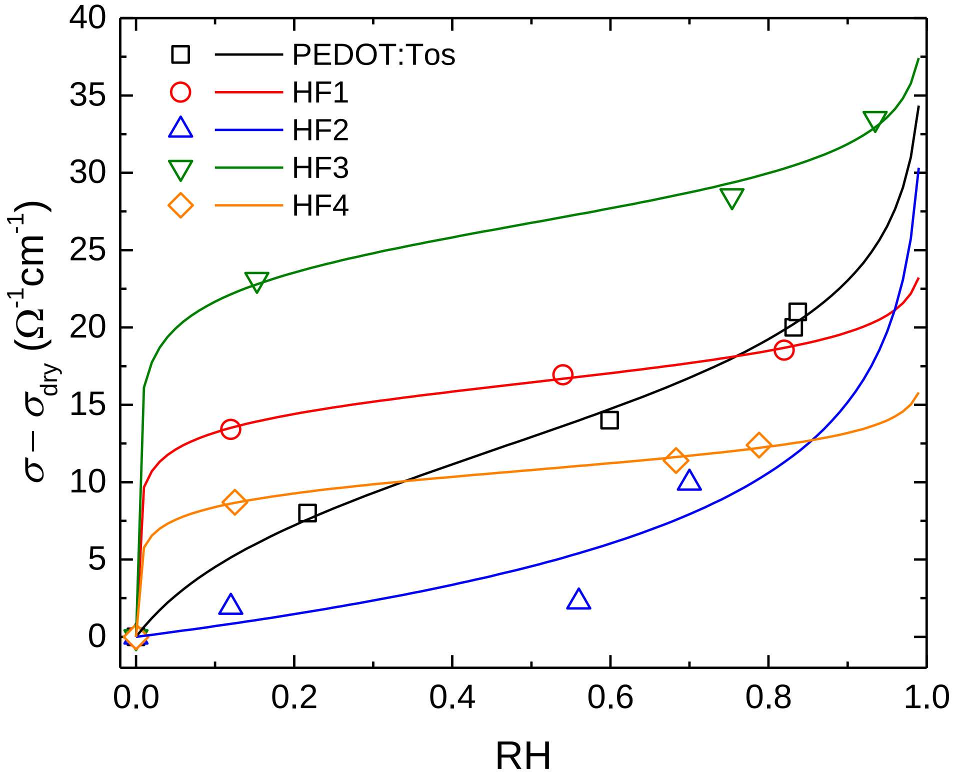
Humidity Effect

	[NP] (cm^{-3})
PEDOT:Tos	0
HF1	$1.5 \cdot 10^{14}$
HF2	$3.0 \cdot 10^{14}$
HF3	$2.2 \cdot 10^{15}$
HF4	$3.0 \cdot 10^{15}$



[NP]: NP density
σ: electrical conductivity
e: electronic charge (1.6×10^{-19} C)
x_w: water molar fraction
β: dimensionless function ($\beta > 0$)

$$\sigma - \sigma_{dry} = \beta([NP]) x_w \left(\sigma_0 + \sigma_1 e^{-[NP]/N_0} \right)$$

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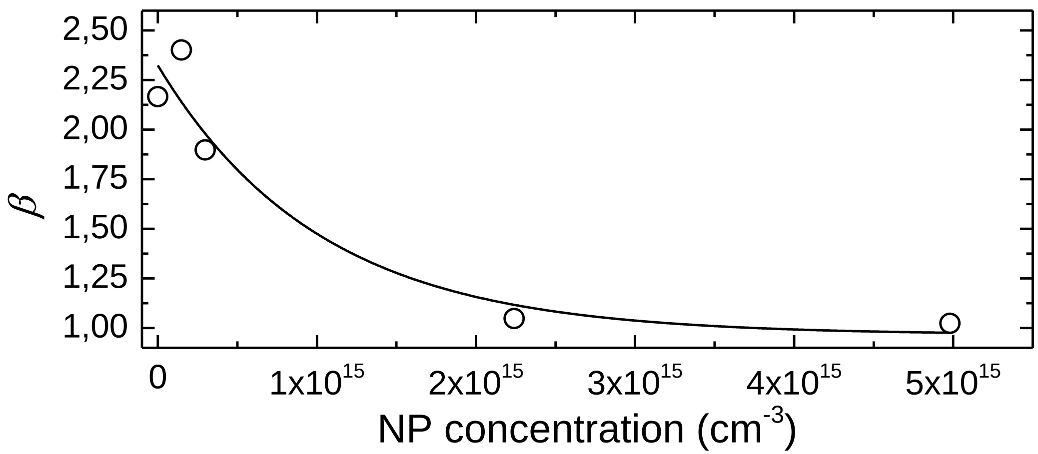
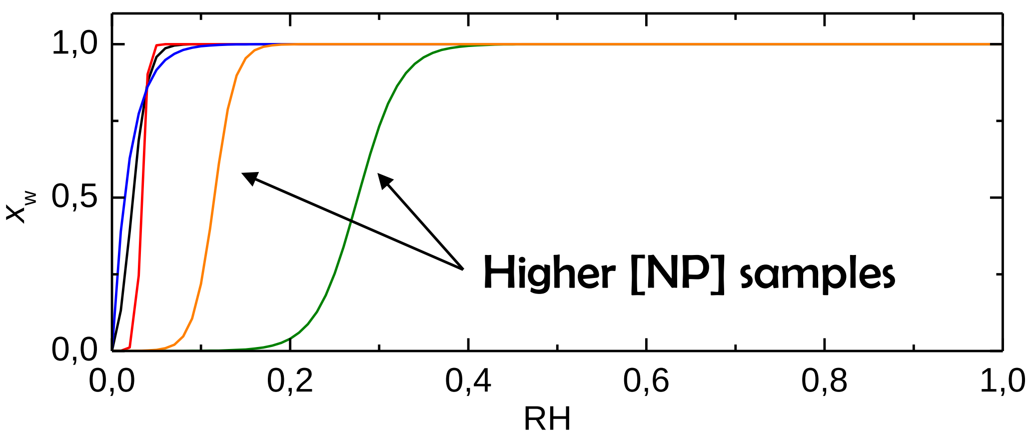
Results

Humidity Effect
Understanding parameters

$$\sigma - \sigma_{dry} = \beta\xi(\mathrm{RH}; \delta_x, x_0)\left(\sigma_0 + \sigma_1 e^{-[NP]/N_0}\right)$$





Parameter β (variation of p due to x_w) exponential decay vs [NP]

Water molecules sequestration by NPs

Broader x_w vs RH curves for higher [NP] samples

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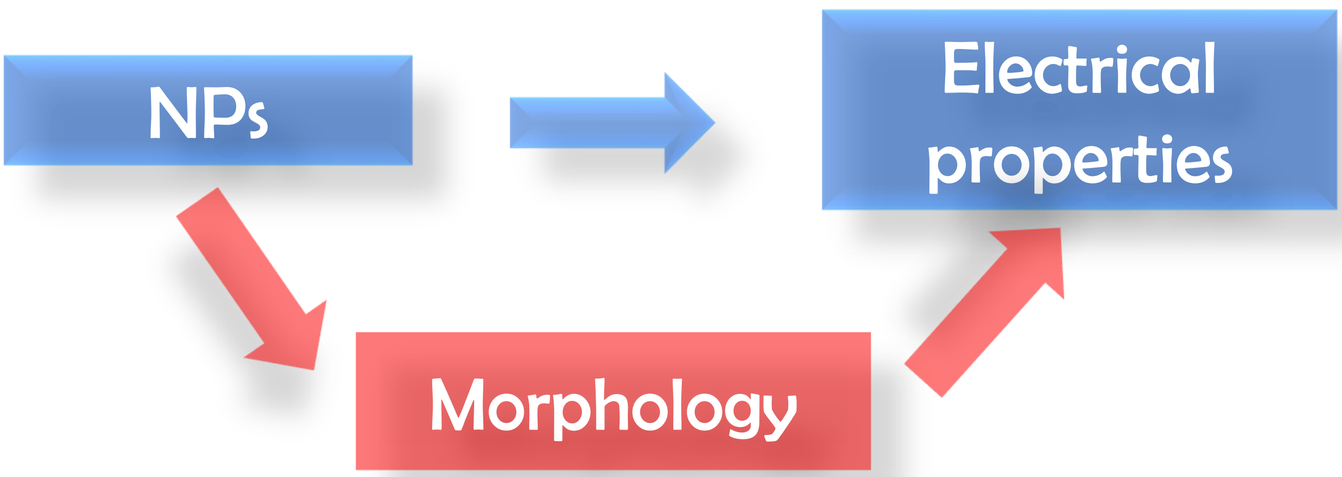
Conclusion

Conclusions and Further Developments

Results obtained:

- A novel protocol to obtain hybrid material CP/INPs has been developed
- Understanding of morphology related aspects of the developed system



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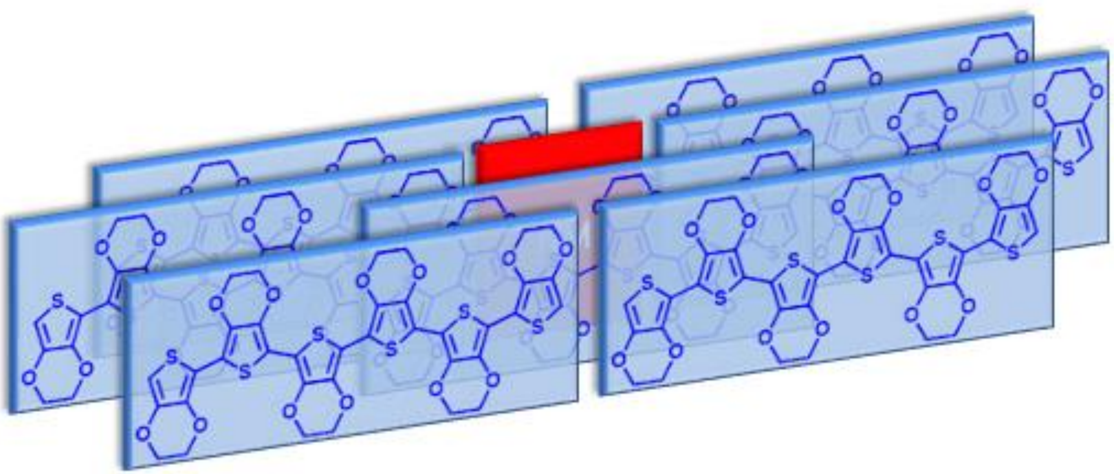
Conclusions and Further Developments

Further Developments:

- Development of a strategy to **avoid nanomaterial detrimental effect** on morphology



1. **Implement polymerization and post-polymerization treatments to favor the rearrangements of NPs (head-to-tail)**
2. **Using 1D nanomaterial**

Thank you for your kind attention!

Aknowledgments

University of Milano-Bicocca

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Electrochemistry Group:
Professor Riccardo Ruffo

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Dr. Silvia Trabattoni

Co-Supervisor:
Dr. Luca Bertini

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SEM Characterization:
Dr. Simone Battiston

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Co-Supervisor:
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