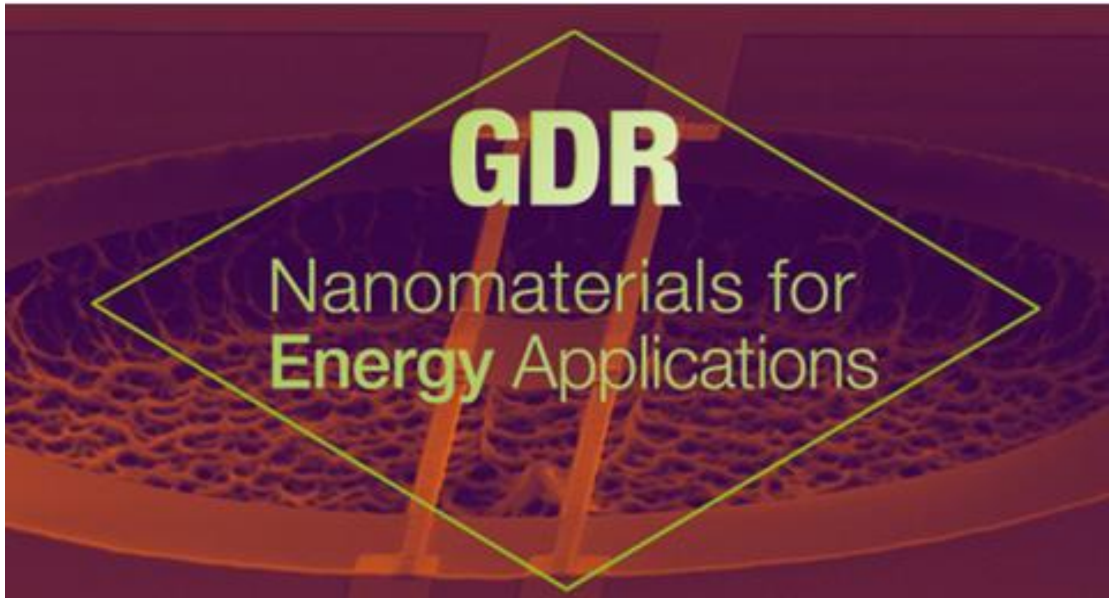
GDR NAME – Workshop Group 3 “energy conversion”

Co-chairs:

Guylaine Poulin-Vittrant, Nicolas Stein, Paolo Bondavalli, Romain Bachelet

Participants:

Rodolphe Vaillon, Andrea Cattoni, Philippe Basset, Bruno Fabre, Jérôme Saint-Martin, Guillaume Savelli, Sylvie Hébert, Sawako Nakamae, Christophe Coutanceau, Marian Chatenet, Maria Tchernycheva, Noëlle Gogneau, Gustavo Ardila, Vincent Consonni



N A M e

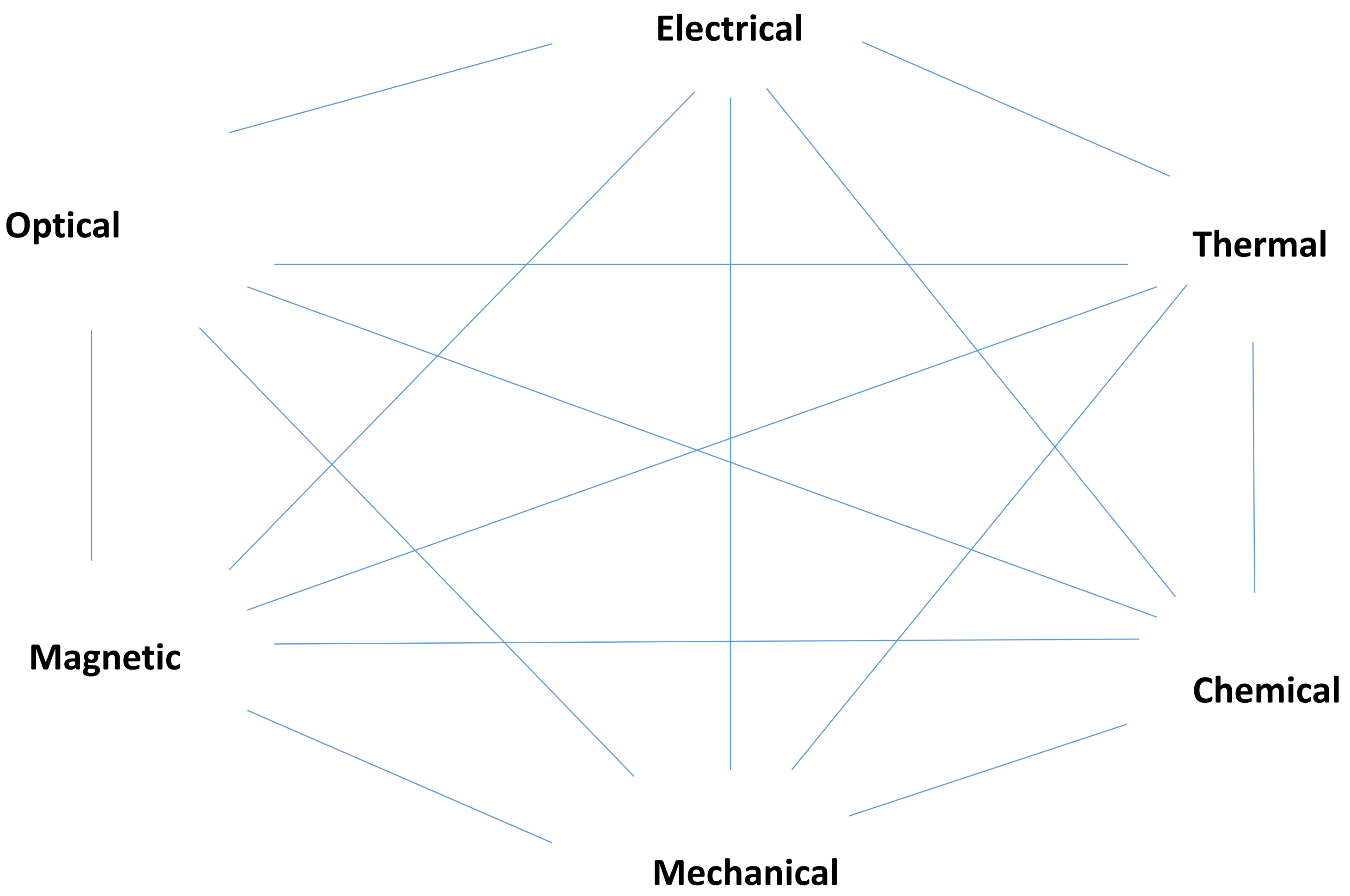
GDR Nanomaterials for Energy Applications

Plenaries May 19-21, 2021 - Visioconference

GDR2086

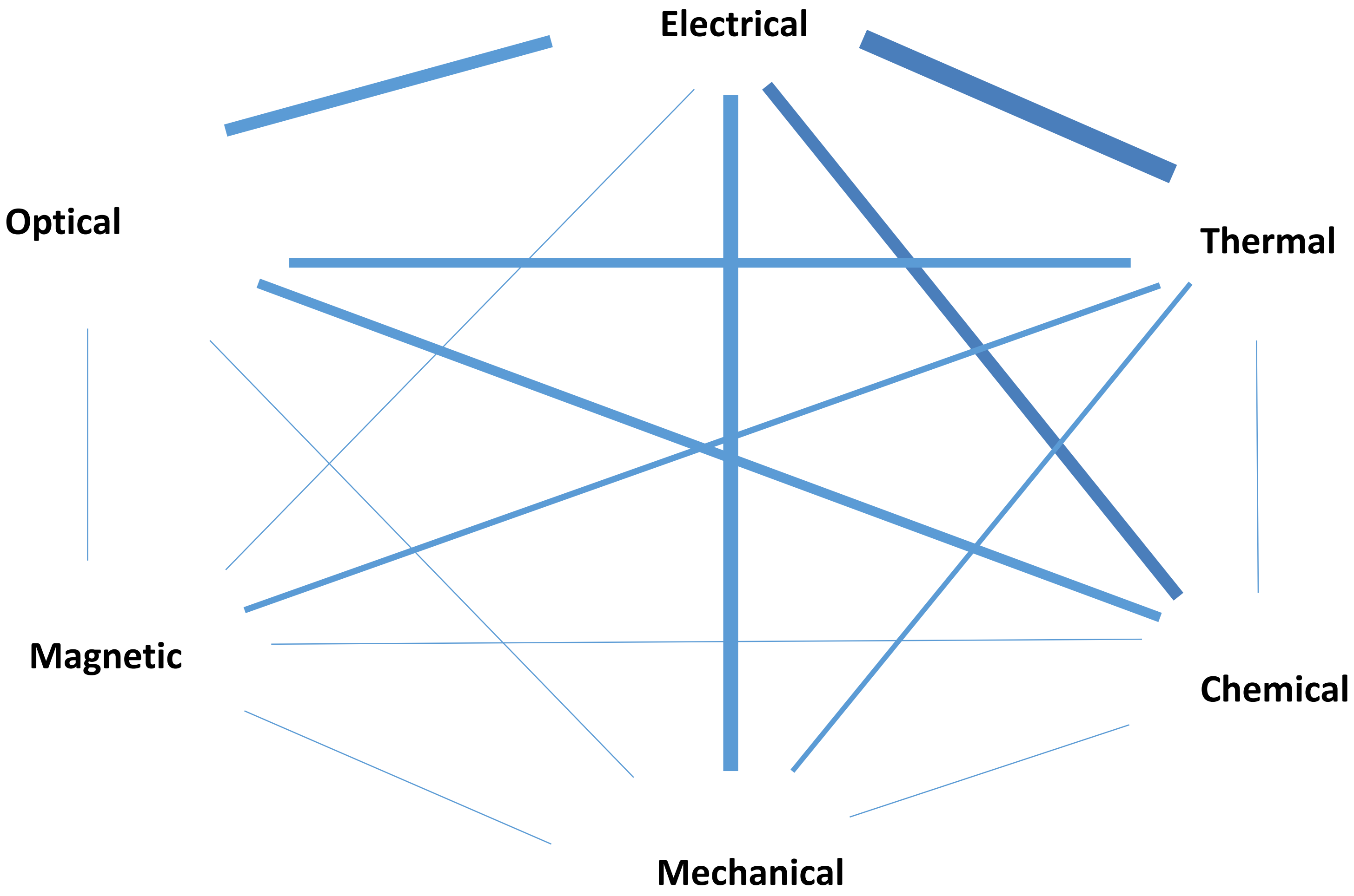
cnrs

Energy conversion overview!

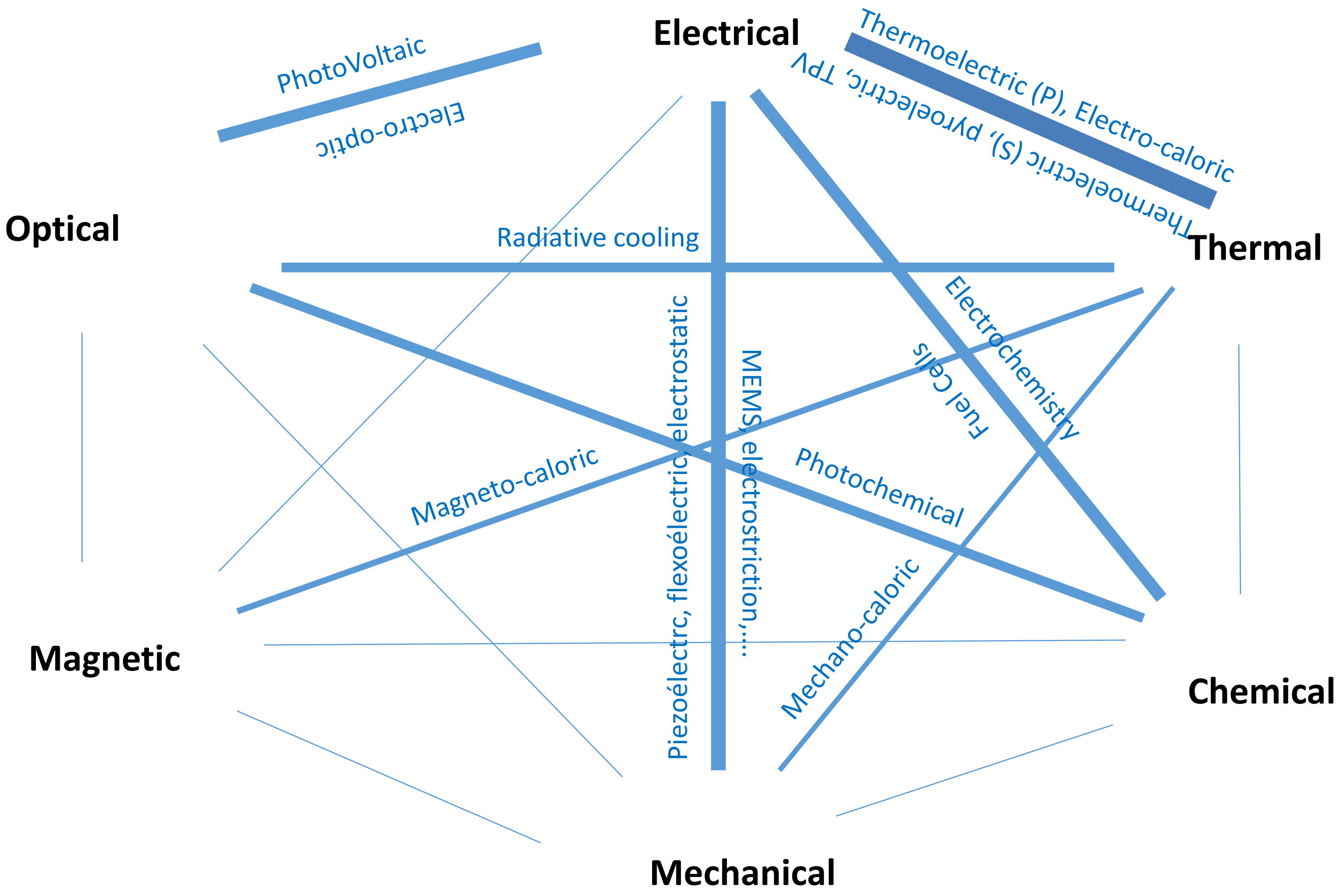


>15 possible conversions or couplings!

Energy conversion overview!



Energy conversion overview!



Outline

1. Thermal ⇔ Electric

1.1. Pyroelectricity et (electro)caloric effect (*Romain Bachelet*)
1.2. Thermoelectricity (*Nicolas Stein*)
1.3. Radiative thermoelectric & Thermo-photovoltaic (*Rodolphe Vaillon*)

2. Optical ⇔ Electric

2.1. Photovoltaic (*Andrea Cattoni*)
2.2. Light Emitting Diodes (*Maria Tchernycheva*)

3. Chemical ⇔ Electric

3.1. Photo-electrochemical (*Bruno Fabre*)
3.2. Fuel cells (*Christophe Coutanceau*)

4. Mechanical ⇔ Electric

4.1. Piezo/flexo-electric (*Guylaine Poulin-Vittrant*)
4.2. Electrostatic (*Philippe Basset*)

5. Hybrides/multiples

5.1. Thermionic - TPV (*Rodolphe Vaillon*)
5.2. Piezo-pyro-tribo-photo-electric (*Romain Bachelet*)

6. General conclusions & perspectives

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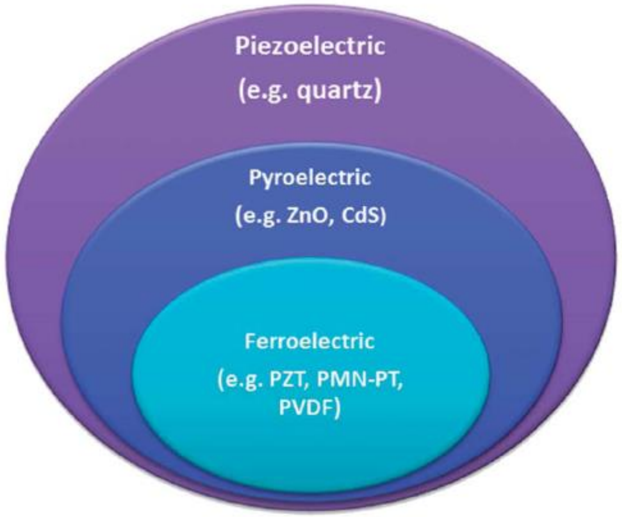
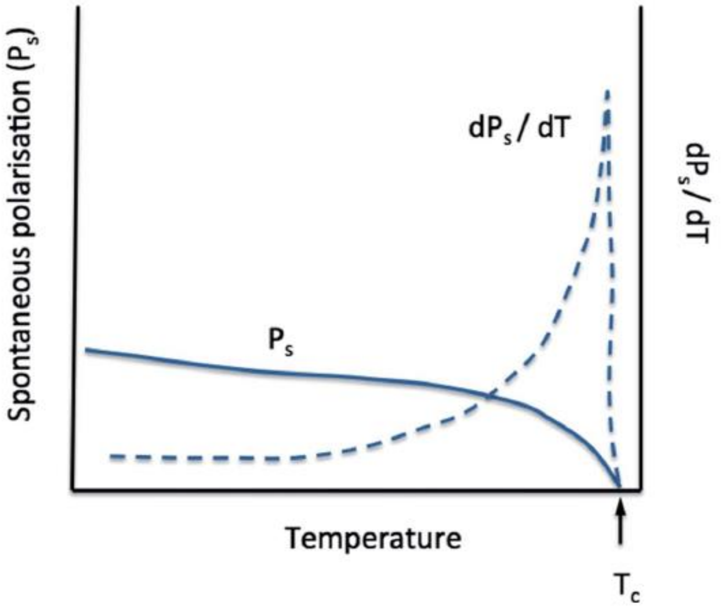
Pyroelectrics

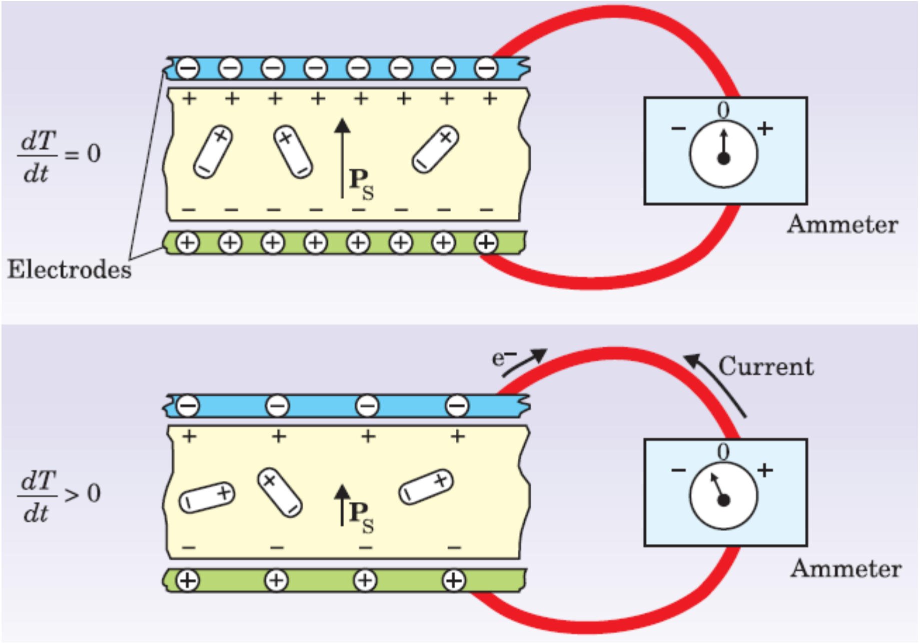
Romain Bachelet

$$p^{\sigma,E} = \left(\frac{dP_s}{dT}\right)_{\sigma,E}$$

Principles







➔ Thermal energy harvesting by dQ/dt from dT/dt (cycling)
➔ No need of thermal differences ⇔ nano thin films OK
➔ No need of 3D structuration for a device

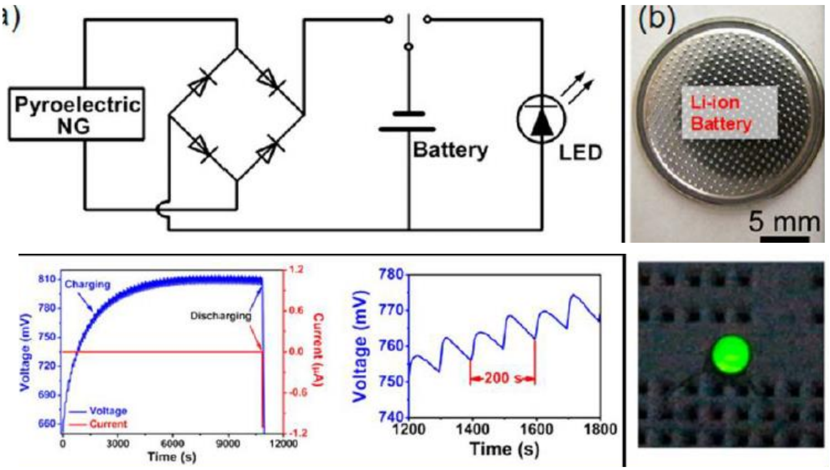
$$i_p = \frac{dQ}{dt} = pA\frac{dT}{dt}$$

FoM: p^2 / ε

Reviews:
Lang, Phys. Today (2005); https://doi.org/10.1063/1.2062916
Bowen, En. Env. Sci. (2015); DOI: 10.1039/c4ee01759e

Best PE materials:
PMN-PT, PZT,…

Polycrystalline PZT films

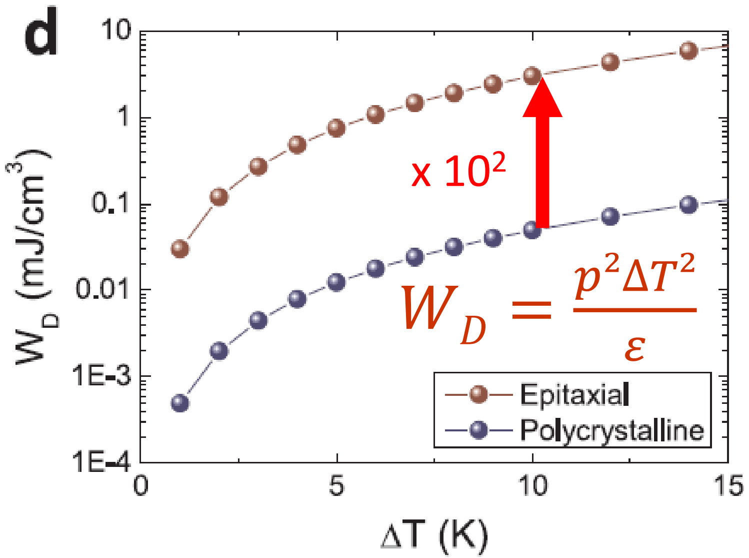


p = −80 nC/cm^{2}K
For “ΔT” = 45 K & dT/dt = 0.2 K/s:

- ➔ output open-circuit voltage ΔU = 22 V
- ➔ short-circuit current density i_p = 171 nA/cm^2
- ➔ maximum power density = 0.215 mW/cm^3

Y. Yang *et al*. (ZL Wang group), Nano Letters (2012);
https://doi.org/10.1021/nl303755m

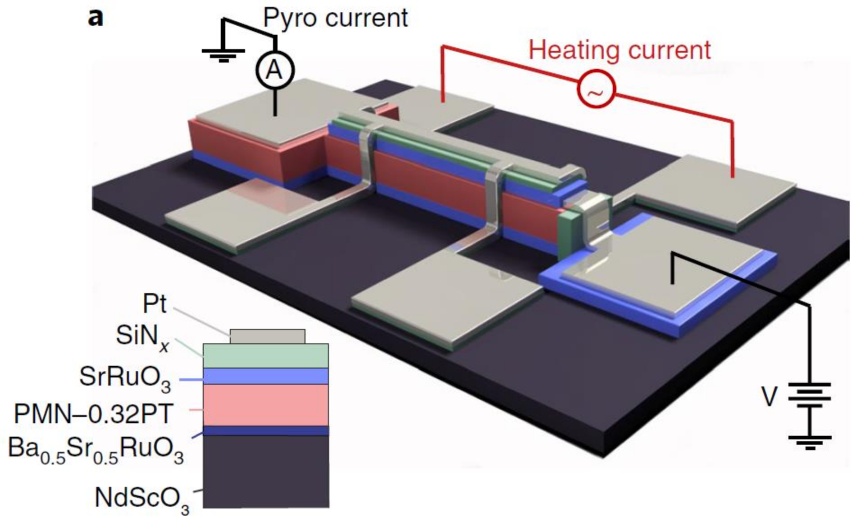
Epitaxial PZT films for enhanced conversion



Decreasing counterbalanced extrinsic effect from DW motions
p = -470 µC/m^{2}K
~1 mJ/cm^3

R. Moalla *et al*., Nano Energy (2017);
http://dx.doi.org/10.1016/j.nanoen.2017.09.001

+ high electric fields with relaxor FE (PMN-PT) films of high p for enhanced conversion



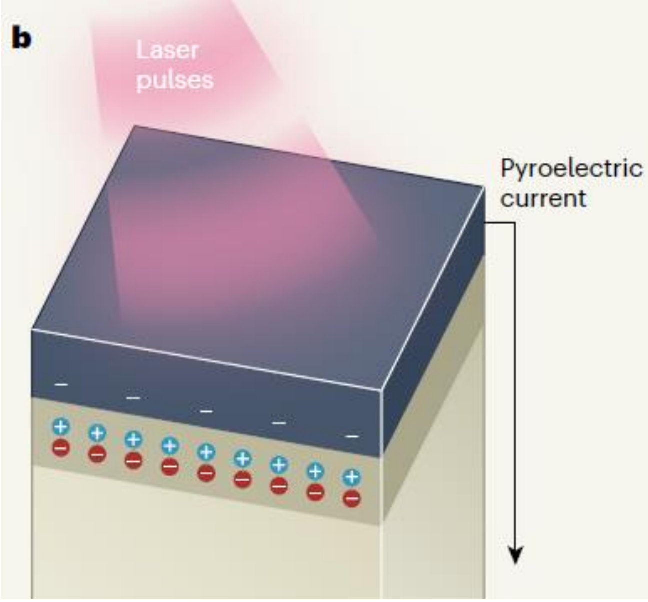
p = -550 µC/m^{2}K
~1 J/cm^3 ⬄ ~500 W/cm^3
19% Carnot efficiency
Equivalent ZT ~ 1.16 (with ΔT=10K)

S. Pandya *et al*., Nature Mater. (2018);
https://doi.org/10.1038/s41563-018-0059-8

Last trends

Nano, down to surface/interface!...
➔ Crystal symmetry breaking and pyroelectric like P(T) effects

Surface polarization feels the heat



e.g. **Pyroelectric surface of non pyroelectric cubic SrTiO3**

➔ Exploiting these effects in other polar dielectric surfaces, articifical nanostructures, heterointerfaces, SLs ?...

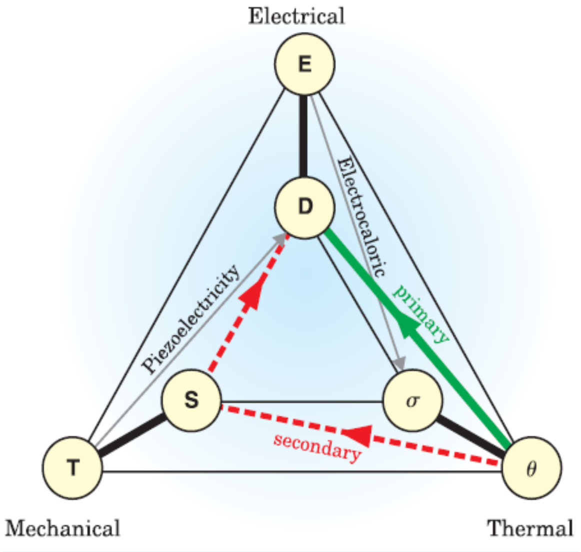
G. Catalan & B. Noheda, Nature (2019); https://doi.org/10.1038/d41586-019-03494-4
E. Meirzadeh, Adv. Mater. (2019); DOI: 10.1002/adma.201904733

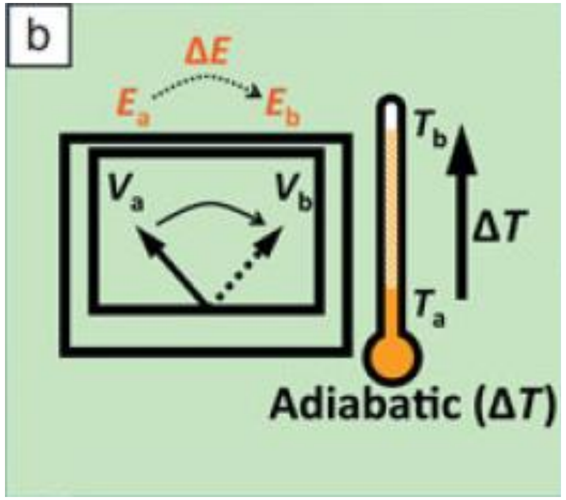
(Electro)Caloric materials

Romain Bachelet

Electrocaloric

On dielectrics (mostly ferroelectrics)





ΔT ~ 10K
with E ~500 kV/cm
Mostly indirect measurements

Electrocaloric effect: A change in applied electric field Δ*E* results in an adiabatic temperature variation Δ *T.*

Mechanocaloric (barocaloroic, elastocaloric,…)

To be completed!...

Inte… materials!

*…alloys can be mitigated by creating a **nanocomposite** that minimizes hysteresis (…0), introducing a ductile grain boundary phase (111, 112), creating fine textured grains via hot extrusion (113), creating **nanoscale** grains by cold rolling and then high temperature aging (114), selecting for good structural compatibility between austenitic and martensitic phases (115), judicious doping (116), and cycling in the middle of the transformation plateau (117).”*

Magnetocaloric

Reviews

J.F. Scott, Annu. Rev. Mater. Res. **(2011)**; DOI: 10.1146/annurev-matsci-062910-100341
M. Valant, Prog. Mater. Sci. **(2012)**; DOI:10.1016/j.pmatsci.2012.02.001
S. Pamir Alpay, MRS Bulletin **(2014)**; DOI: 10.1557/mrs.2014.256
X. Moya *et al.*, “*Caloric materials near ferroic phase transitions*” Nature Mater. **(2014)**; https://doi.org/10.1038/nmat3951
X. Moya and N. D. Mathur, “*Caloric materials for cooling and heating*”, Science **(2020)** (Review); DOI: 10.1126/science.abb0973

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6. General conclusions & perspectives

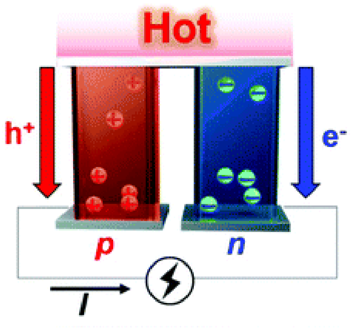
Conversion thermique ⇔ électrique

Thermoélectricité

Romain Bachelet
INL, EC Lyon, CNRS
Paolo Bondavalli
ThalesGroup
Sylvie Hébert
CRISMAT, ENSICAEN, CNRS
Sawako Nakamae
SPEC/IRAMIS/CEA, CNRS
Jérôme Saint Martin
C2N, université Paris Saclay, CNRS
Guillaume Savelli
LITEN, CEA
Nicolas Stein
IJL, université de Lorraine, CNRS

Jérôme Saint Martin

Thermoelectrics



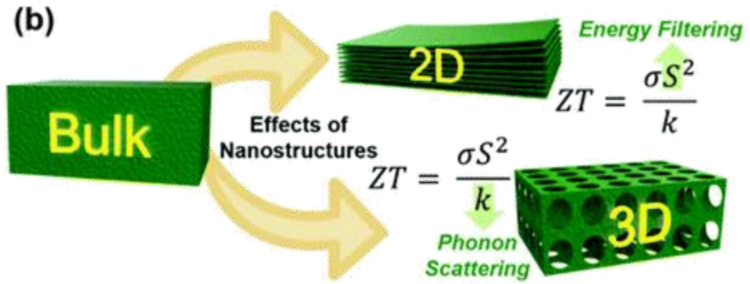
Nanoscale, 2019,11, 19684

Principle
Direct conversion of thermal flux into electrical power

Efficiency: $$\eta_{\max} = \eta_{Carnot} \cdot \frac{\sqrt{ZT+1}-1}{\sqrt{ZT+1}+\frac{T_{cold}}{T_{hot}}}$$

Figure of merit: $$ZT = \frac{T\sigma S^2}{k_{ph}+\kappa_e}$$

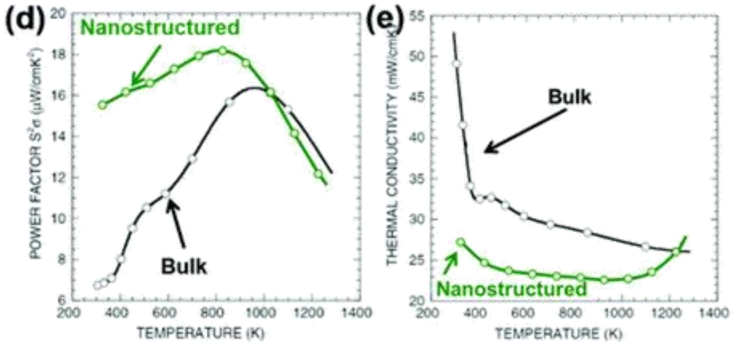
Typical ZT_{max} 1 – 2
Microdevices = Output power range ≈ 1-100 µW/cm²
with mV Seebeck voltage
for ΔT 1-20K.



Nanoscale, 2019,11, 19684

Nanostructuring

- k_{th} lowering by reducing phonon mean free path
- S improvement by energy filtering (quantum confinement)



L. D. Hicks and M. S. Dresselhaus, Phys. Rev. B **47**, 12727 (1993).

D.M. Rowe (Ed.), Thermoelectrics and Its Energy Harvesting. Modules, Sytems and Applications in Thermoelectrics, CRC Press 2012–2013

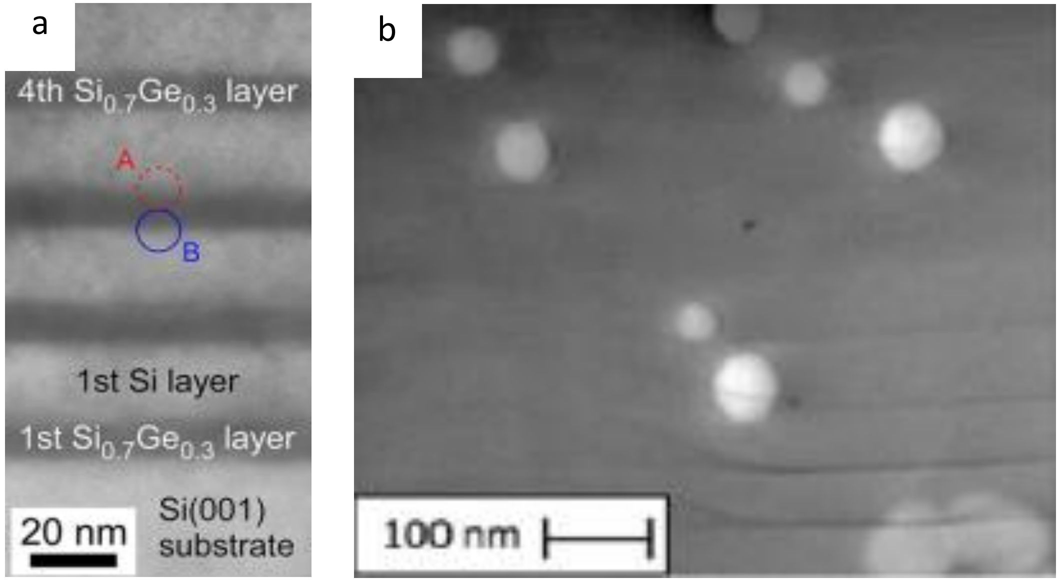
Mao, J., Liu, Z. & Ren, Z. Size effect in thermoelectric materials. *npj Quant Mater* **1,** 16028 (2016).

Guillaume Savelli / Romain Bachelet

Superlattices (SL) and quantum dot superlattices (QDSL) for an improvement of TE performances

SL and QDSL have been used for thermoelectric conversion since the early 2000’s and applied for many TE families :

- Bi_2Te_3/Sb_2Te_3[1,2], SiGe/Si[3], PbS/GeTe[4], GaAs/Ge[5], Al_2O_3/ZnO[6], $SrTiO_3$-based[7] for SL
- $SiGe/TiSi_2$[8], InGaAs/ErAs[9,10], PbTe/PbSeTe[11] for QDSL

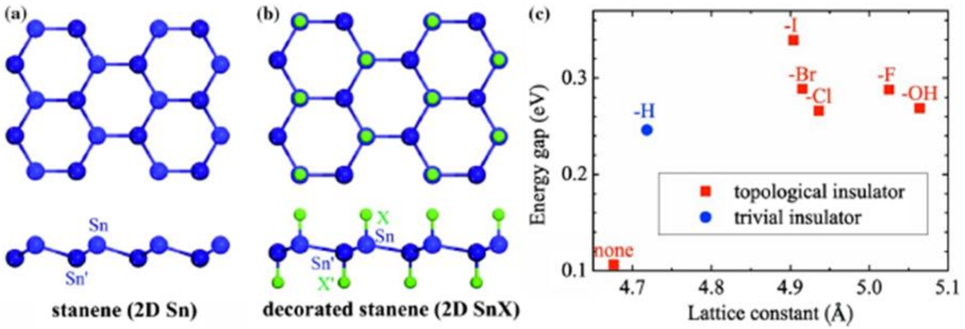


a) Cross-sectional HRTEM image of a SiGe/Si SL[3];
b) Cross-sectional STEM/HAADF image of a $SiGe/TiSi_2$ QDSL[7]

- The nanostructuration acts mainly by reducing the thermal conductivity, with sometimes a simultaneous increase of the power factor
- In addition to doping and stoichiometric considerations, key parameters are layers thickness (SL) and nanoparticles size and concentration (QDSL)

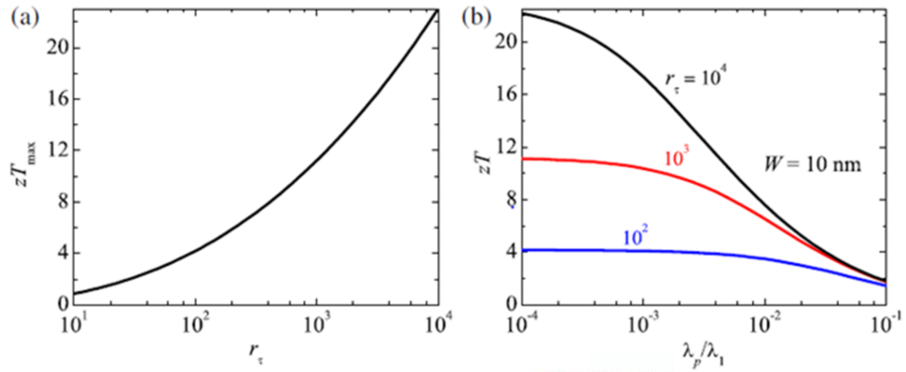
1 - R. Venkatasubramanian et al., Nature 413, 597 (2001
2 - R. Venkatasubramanian et al., Appl. Phys. Lett. 75, 1104 (1999)
4 - A. Ishida et al., Jpn. J. Appl. Phys. 55, 081201 (2016)
5 - R. Jia et al., Appl. Phys. Lett. 110, 222105 (2017)
6 - W. Y. Lee et al., J. Phys. Chem. C 123, 14187 (2019)
7 - A. I. Abutaha et al., Chem. Mater. 27, 2165 (2015)
8 - G. Savelli et al., J. Phys. D: Appl. Phys. 53, 445101 (2020)
9 - J. M. Zide et al, Appl. Phys. Lett. 87, 112102, (2005)
10 - G. Zhen et al., J. Appl. Phys. 101, 034502 (2007)
11 - T. C. Harman et al., Science 297, 2229 (200

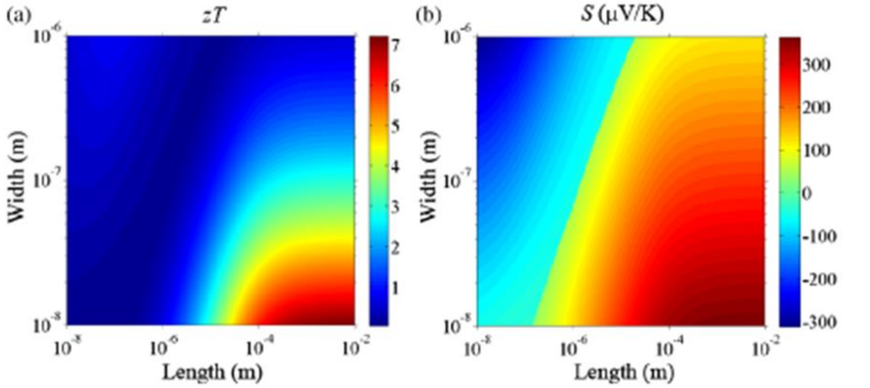
2D topological insulators for thermoelectricity



a) Stanene configuration with its typical low-buckled structure.
b) Decorated stanene in case of sp3 hybridization.
c) Energy gap as a function of the lattice for different decoration using different atoms

a) Maximum theoretically value for zT in case of 2D TIs as a function of the ration between the scattering times of the edges states inside and outside the gap.
b) zT as a function of the rations between the mean free path of phonons and of the inelastic mean free path of edge states





a) zT value as a function of the length, L, and Width, W, of the nanoribbon.
b) Seebeck parameter as a function of L and W.

C. L. Kane and E. J. Mele. Phys. Rev. Lett. 95, 226801 (2005)
Xu, Y. et al. Phys. Rev. Lett. 112, 226801 (2014).
Y.Xu, et al. PRL 111, 136804 (2013).

SOC proportional to Z^4

Nicolas Stein

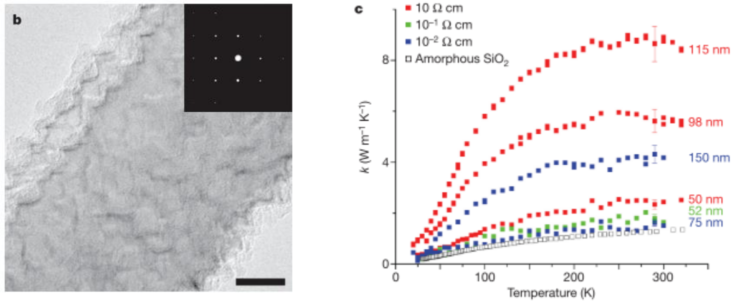
1D nanostructures for TE energy conversion

Charge transport : quantum confinement effects, semimetal to semiconductor transition and surface engineering.

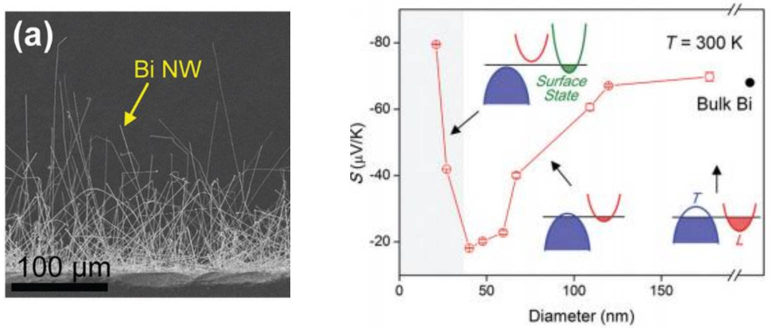
Phonon engineering : phonon scattering with the surfaces and with the surface roughness.

Main factors : their geometry (diameter, surface roughness), their microstructure and their composition (chemical modulations, core-shell)

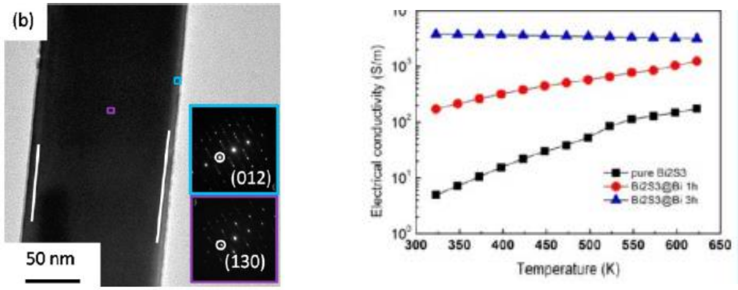
applied to a wide range of semiconductors but the main outstanding results concern Si-based and bismuth telluride-based compounds.



Rough Si NW
A. I. Hochbaum Nature 451, 163 (2008).



Bi NWs by Off On method
J. Kim, *Nanoscale* **7**, 5053 (2015).



Bi_2S_3@Bi NWs Ge et al., ACS AMI 9, 4828 (2017).

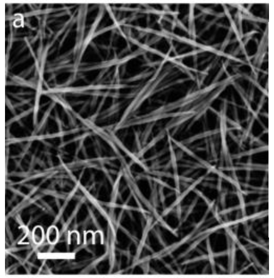


TABLE 1. Room Temperature Thermoelectric Properties of Te/Pedot:PSS Nanocomposite and Control Films

system	σ (S/cm)	S (μV/K)	$S^2\sigma_{max}$ (μW/(m K^2))	κ (W/(m K))	ZT_{max}
hybrid	19.3(±2.3)	163(±4)	70.9	0.22−0.30[a]	0.10
PEDOT:PSS	1.32(±0.12)	18.9(±0.2)	0.05	0.24−0.29	6×10^{-5}
Te NWs	0.08(±0.03)	408(±69)	2.7	2[b]	4×10^{-4}

film Te NWs PEDOT:PSS See *Nano letters* **10**, 4664 (2010).

Thin films of conducting polymers : PEDOT:PSS, P3HT, PANIs, …

Sylvie Hébert

Nanostructuration of bulk materials

Main parameters for energy filtering and / or thermal conductivity reduction:

- Preparation of samples made by ball milling / mechanical alloying
- Nanoinclusions, voids
- Nanocomposites
- Grain / grain boundaries design
- Solution processed synthesis for bottom up approaches

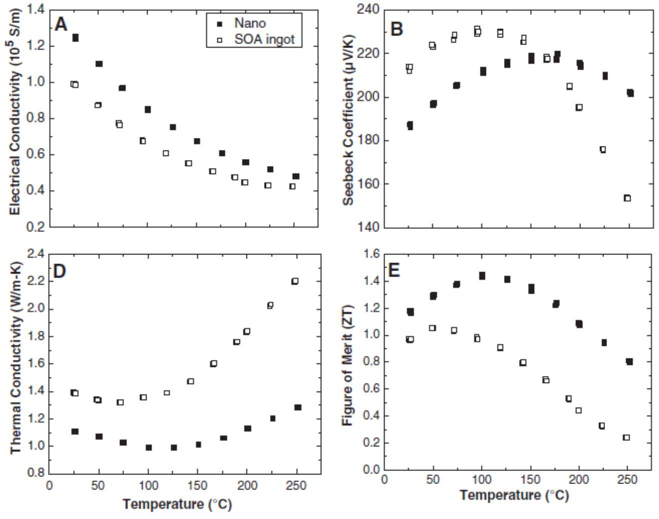
Has been applied in most families of thermoelectric materials:

Bi_2Te_3, PbTe, SiGe, silicides, clathrates, Half-Heusler, oxides…

The impact of nanostructuration depends on the materials characteristics,
on the relative mean free path of electrons and phonons

4500 articles since ~ 2000
Impossible to make an exhaustive review!

N. Neophytous et al., EPJB93, 213 (2020), D. Beretta et al. Materials Sci. Eng. 138, 210 (2019), S. Ortega et al., Chem. Soc. Rev. 46, 3510 (2017) + …



B. Poudeu et al., Science 320, 634 (2008)

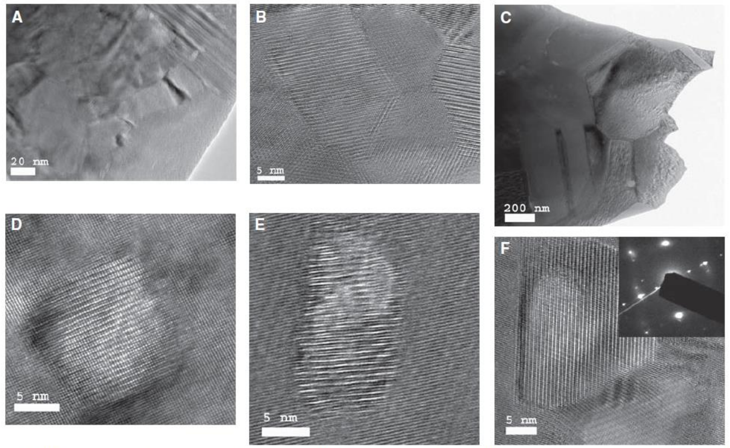
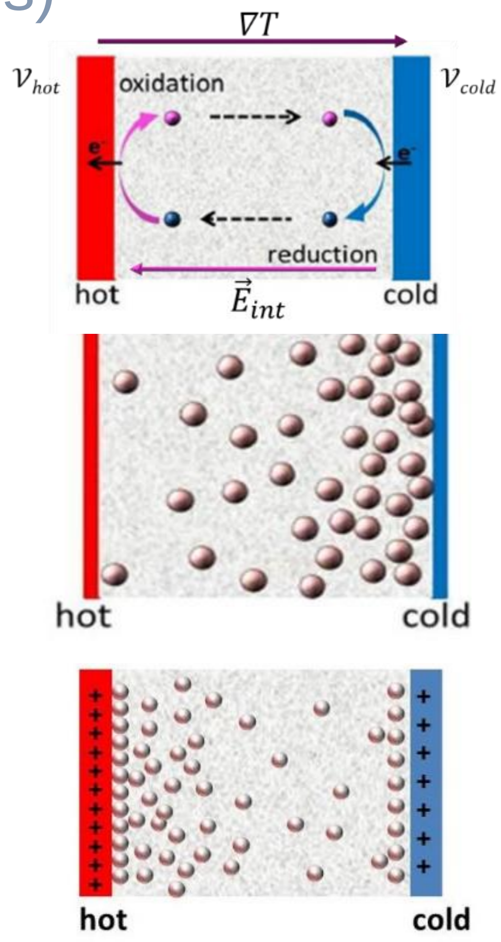


Fig. 3. TEM images showing the microstructures of a hot-pressed NC bulk sample. (**A**) Low-magnification image showing the nanograins. (**B**) High-magnification image showing the nanosize, high crystallinity, random orientation, and clean grain boundaries. (**C**) Low-magnification image showing larger grains. (**D** and **E**) High-magnification images showing the nanodots in the matrix without boundaries (D) and with small-angle grain boundaries (E). (**F**) High-magnification image showing Te precipitate in the matrix. SAED pattern (inset) shows the Te phase of the precipitated nanodot in the matrix.

Pioneering work : **p type $Bi_{0.4}Sb_{1.6}Te_3$**

Nanofluid thermoelectrics (thermoelectrochemical cells)



- Multiple thermoelectric origins:
  1. Thermogalvanic effect (redox reactions) ~1-3mV/K
  2. Thermodiffusion effect (nanoparticles) ~100-200 μV/K
  3. T-dependent electronic double-layer formation (electrodes) ~variable
- Latest trends
  - Ionic liquids & redox (higher Se, σ, wider operational temperature range)
  - Nanofluids (higher Se, σ wider operational temperature range)
  - Nanostructured and carbon-based electrodes (higher σ, cheaper material)
  - Prototype demonstration (~10W/m^2 in water-based cells)
- Main parameters/materials and influence of nanomaterials
  - Nanostructured electrodes ➔ Enhancing effective surface area
  - Nanoparticle/solvent interface ➔ NPs' dynamic effective charge, diffusion coefficient, entropy of transfer, Seebeck coefficient

SWOT analysis

STRENGTHS
- Decoupling TE parameters with low dimensions
  - Energy filtering
  - Reducing lattice thermal conductivity

OPPORTUNITIES
- Thin film Heusler alloy *
- 2D nanostructures
- Hybrid systems with conducting polymer and inorganic nanostructures

WEAKNESS
- measurement challenges for nanostructures (ZT)

THREATS
- need of reliable devices including nanostructures

*Hinterleitner, B. alloy. *Nature* **576,** 85–90 (2019)

1. Thermal ⇔ Electric

2. Optical ⇔ Electric

3. Chemical ⇔ Electric

4. Mechanical ⇔ Electric

5. Hybrides/multiples

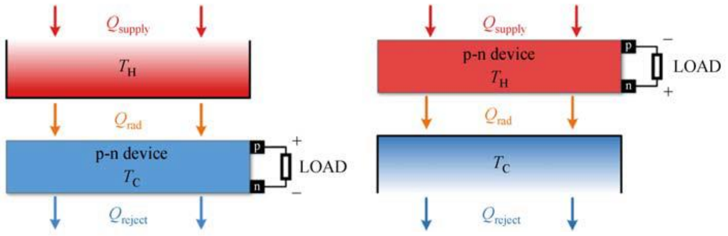
6. General conclusions & perspectives

Radiative Thermoelectric Energy Converters

Rodolphe Vaillon

- Concepts: (Tervo et al., Front. Energy, 2018)

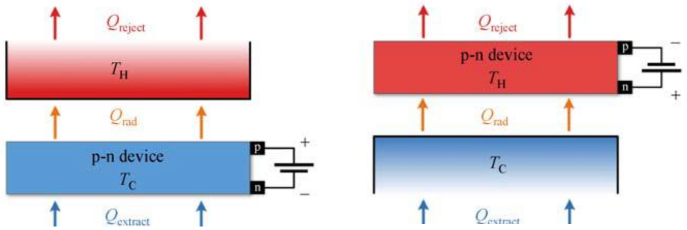
Thermal radiation → Electrical



(a) Thermophotovoltaics (b) Thermoradiative

concept proposed in: (a) the 50's, (b) 2014

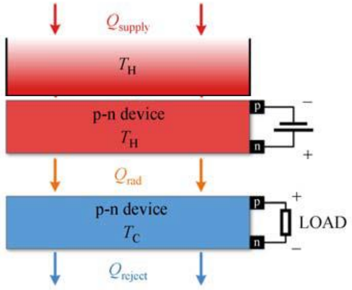
Electrical luminescence → Refrigeration



(c) Electroluminescent (d) Negative electroluminescent

(c) 1957, (d) 1985

Thermal radiation + elec. lumin. → Electrical



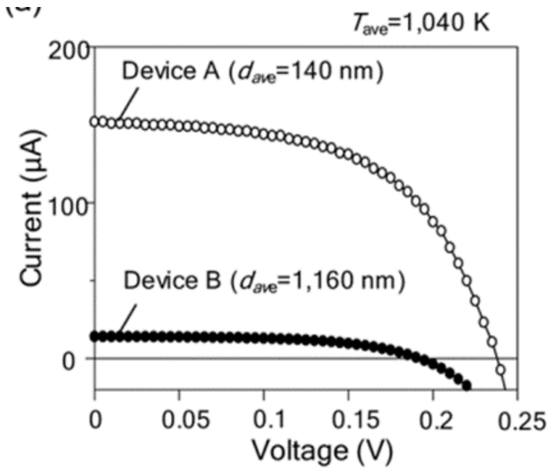
(e) Thermophotonics 2003

(Harder & Green, Semicond. Sci. technol., 2003) far field
(Zhao et al., Nano Lett., 2018) near field

- Nanomaterials: nanostructures for thermal radiation control, including the gap between the hot and cold bodies (near-field effects)

- Last trends: → first convincing experimental demonstrations with near-field effects

(a) NF-TPV: (Fiorino et al., Nat. Nanotech. 13, 806–811, 2018; Inoue et al., Nano Lett. 19(6), 3948–3952, 2019; Bhatt et al., Nat. Comm., 2020; Lucchesi et al., arXiv, 2019); (b) None; (c) None; (d) NF-NEL: (Zhu et al., Nature, 2019); (e) None.



→ modelling with near-field effects: all active areas, mostly (a) since the 2000's.

- Focus on (a) thermophotovoltaics (upcoming slide)
- Basic research
- Needs for the future: more experimental demonstrations, joint opto-electrical-thermal design, 2&3D effects

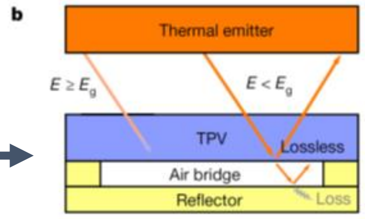
Thermophotovoltaics

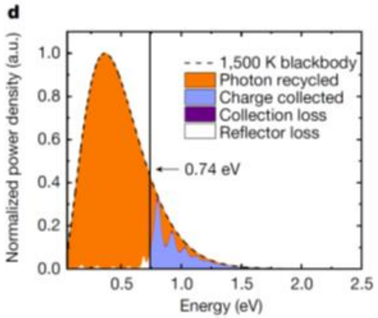
Rodolphe Vaillon

- Last trends in the domain:

Record efficiency (29-32%) research cells by maximizing photon recycling toward the emitter with broadband near-perfect reflectors

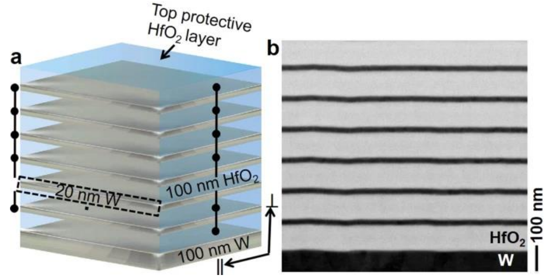
(Omair et al., PNAS 116(31), 15356-15361, 2019; Fan et al., Nature 586, pages237–241, 2020) →



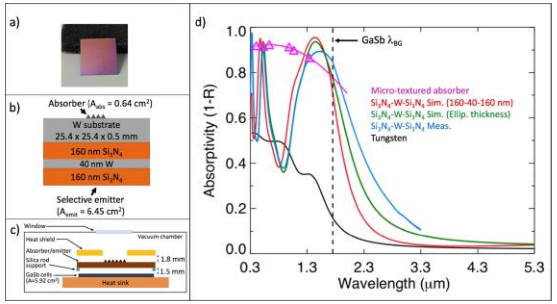


Stable high-temperature selective emitters

(Sakakibara et al., J. Photon. Energy 9(3), 032713, 2019)



(Chirumamilla et al., Sci. Reports 10, 3605,, 2019)



(Bhatt et al., Solar Energy 197, 538-545, 2020)

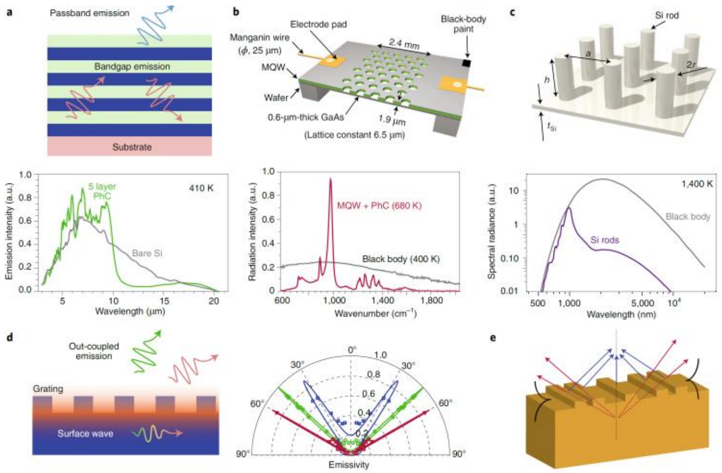
- Performances: electrical power density < 1 W.cm^{-2}

efficiency: (far field) ~32% (device), ~11% (system); (near field) ~14% (cell at 77 K)

- Basic research (very little commercial products)
- Needs for the future: emerging advanced related concepts (earlier slide), up-scaling (systems), improvements: very-low bandgap cell vs. emitter at larger temperatures

- Nanomaterials: nanophotonic engineering of the thermal radiation emitters (more recent trend: of the cell as well)

(Baranov et al., Nat. Materials 18, 920–930, 2019)



Wave effects (interferences, diffraction, polaritons), structure effects (multilayers, photonic crystals, metamaterials)

(Boriskina et al., Nanophotonics 18, 073004, 2016; Ben-Abdallah & Biehs, Z. Naturforsch. 74, 689-696, 2019)

Thermophotovoltaics

Analysis SWOT

FORCES

- Design (thermal radiation modeling of emitters, radiation-electrical-thermal modeling)
- Nanoscale radiation experiments
- Advanced concepts

WEAKNESSES

- Not many labs working on this topic
- In particular for the (nano-)fabrication of TPV cells and emitters, measurement of radiative properties at high temperature, thermal energy harvesting and storage at high temperature

OPPORTUNITIES

- From modeling to fabrication of emitters
- From devices to systems
- Strong solar PV community in France
- Networking

RISKS

- Stagnation (even decline) with an insufficient critical mass of French teams

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1.2. Thermoelectricity (*Nicolas Stein*)
1.3. Radiative thermoelectric & Thermo-photovoltaic (*Rodolphe Vaillon*)

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2.2. Light Emitting Diodes (*Maria Tchernycheva*)

3. Chemical ⇔ Electric

3.1. Photo-electrochemical (*Bruno Fabre*)
3.2. Fuel cells (*Christophe Coutanceau*)

4. Mechanical ⇔ Electric

4.1. Piezo/flexo-electric (*Guylaine Poulin-Vittrant*)
4.2. Electrostatic (*Philippe Basset*)

5. Hybrides/multiples

5.1. Thermionic - TPV (*Rodolphe Vaillon*)
5.2. Piezo-pyro-tribo-photo-electric (*Romain Bachelet*)

6. General conclusions & perspectives

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Introduction: **Optique → Electrique : Photovoltaics**

Andrea Cattoni (C2N)

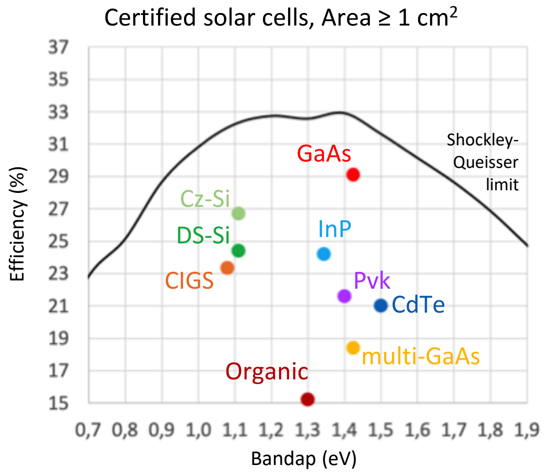
Nanotechnology and Nanoscience can be used to for example to

- Synthetized absorber materials with different physical properties, shapes or funtionalities (quantum absorbers, Heterocontacts etc.)
- Facilitate technology hybridization (III-V on Si integration using selective growth)
- "Bend light" to improve light absorption and thus carrier collection (optically thick / electrically thick solar cells)

with the ultimate goal to overcome Shockley–Queisser limit AND/OR improve efficiencies AND/OR reduce costs.

Subtopic: **Light trapping in solar cells**

Andrea Cattoni (C2N)



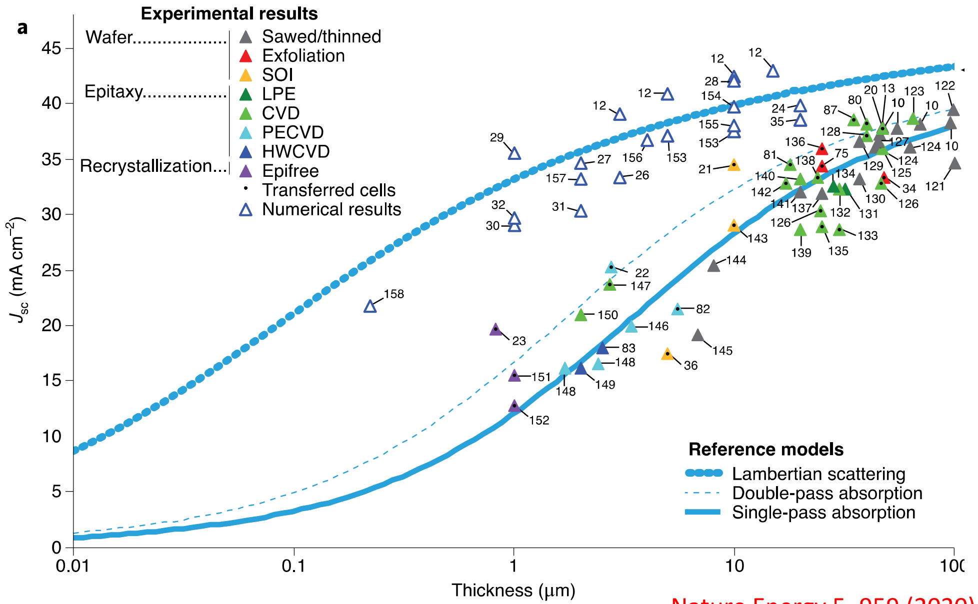
Adapted from:
Solar cell efficiency tables (version 57),
Prog Photovolt Res Appl. 29, 3 (2021)

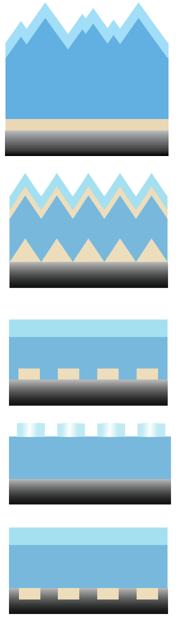
While the efficiencies of state of the art solar cells are very close to the Shockley–Queisser limit

....

they essentially operate at the single-pass absorption: light-trapping has the potential to reduce the solar cell thickness of at least a factor 10

State of the art for c-Si solar cells





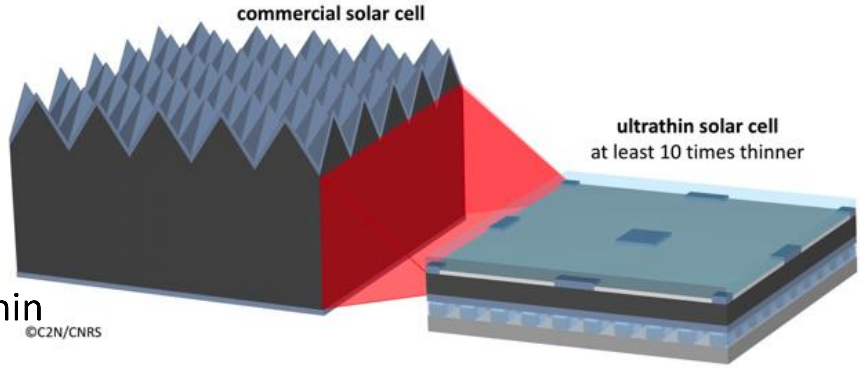
Nature Energy 5, 959 (2020)

Potential

- Improve throughput / cost-reduction (CIGS, CdTe)
- Improve lifetime & power production: III-V (space), CIGS, Si, CdTe (reduced heating with a mirror)
- Improve carrier collection in defective absorber materials (new/cheaper absorber materials)

Challenges

- Low-cost and large-surface areas Nano-structuration
- Fabrication of ultra-thin absorbers
- Carrier collection in ultra-thin junctions



Subtopic: **Nanowire based solar cells**

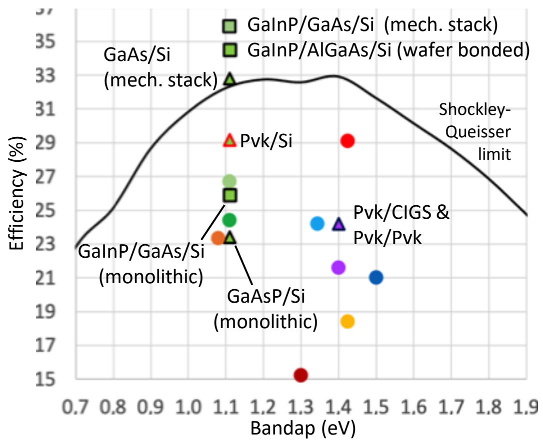
Andrea Cattoni (C2N)

- Si-wafer based PV: 95% share (2017)
- State of art efficiency (26.7%) approaching the th. limit of Si (29%)

→ **Priority:** 2-T Si-based tandem solar cell (η > 30%), the challenge:

- Wide-bandgap (1.7 eV) top cell ≥ 20% and areal cost < \$100 m^{-2}
- Facile integration on Si bottom cell, little coupling loss, durability (25 year)

Nature Energy 3, 747 (2018)

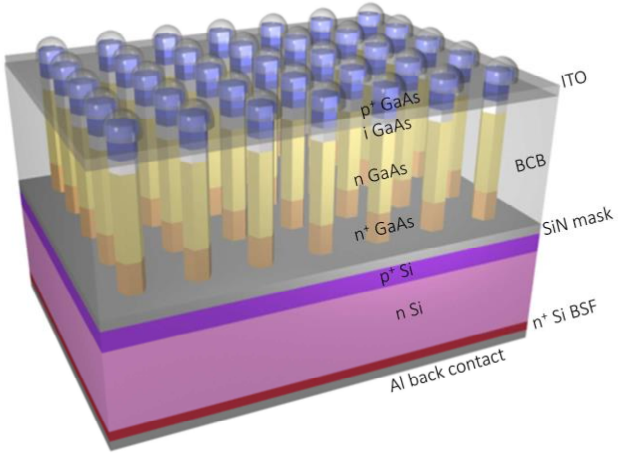


Adapted from:
Solar cell efficiency tables (version 57),
Prog Photovolt Res Appl. 29, 3 (2021)

The technology used for the top cell is far from being established: III-V → work but expensive (substrate!) / Pvk -> poor stability/Lead...

Potential: defect-free III-V NWs can be grown on mismatched substrates such as Si

→ no need to expensive III-V substrate
→ simple / no-losses integration



State of the Art:

- GaAs NWs on GaAs substrate: 15.3%

IEEE J. Photovoltaics 6, 185 (2016)

- GaAs NWs tandem on Si: 11.4%

Nano Letters 15, 7217 (2015)

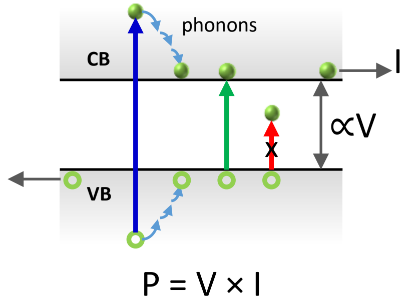
Challenges: Low efficiencies (recent technology) BUT <u>not intrinsically limited by material quality</u>:

- Low-cost nano-structuration for selective area growth
- Control of the junction formation at the nanoscale
- Nanoscale characterization (doping, junction formation)
- Device fabrication: billions of nanoscales solar cells interconnected (TCO/III-V contact etc.)

Subtopic: **Hot carrier solar cells**

Andrea Cattoni (C2N)

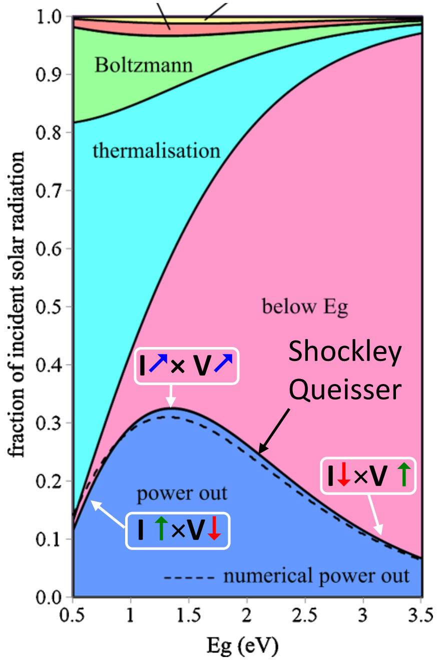
Fundamental losses



1) **Thermalization** of photo-generated carriers → phonon

2) **Not absorption**

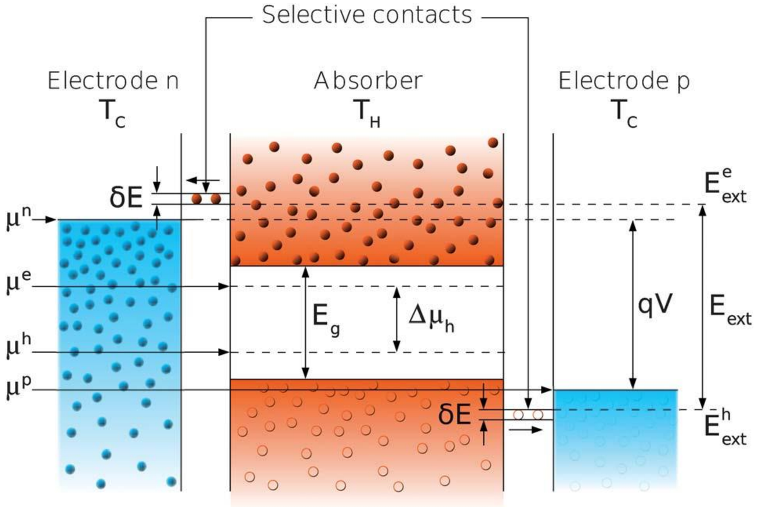
Prog. PV: Res. Appl. 19, 286 (2011)



Hot carrier solar cell

1) Collect hot photo-generated carriers (prevent thermalization → **high V_{OC}**)

2) Small bandgap semiconductors (high absorption → **high J_{SC}**)



Potential

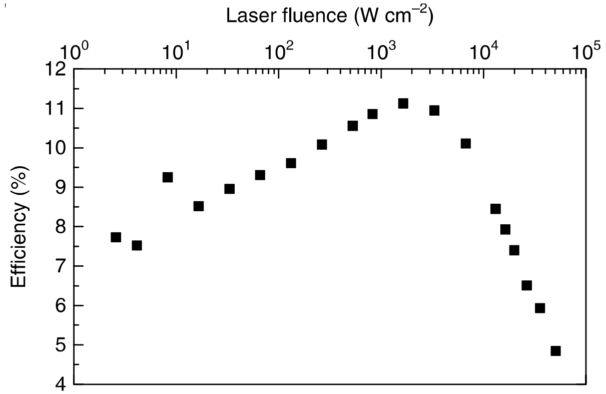
Exceeding SQ limit with a simpler architecture as compared multi-junction solar cells

Challenges

1) Material with large optical/acoustic bandgap to achieve *phonon bottleneck* (Quantum structures)

2) Energy selective contacts (resonant tunneling etc.)

3) Obtain high carrier temperatures (Concentration + Light trapping) and correctly measure them (PL + generalized Planck's law)



State of the art

- "Quantitative experimental assessment of hot carrier-enhanced solar cells at room temperature" Nature Energy 3, 236 (2018)
- "Exploiting intervalley scattering to harness hot carriers in III–V solar cells" Nature Energy 5, 336 (2020)

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Nanowire light emitting diodes for high efficiency solid state lighting

M. Tchernycheva

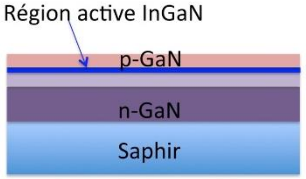
Issues of standard nitride LEDs :

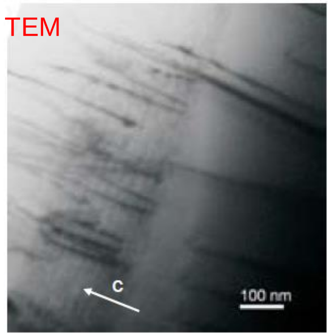
- Structural defects
- Efficiency droop under high injection

Nanowire core/shell LED:

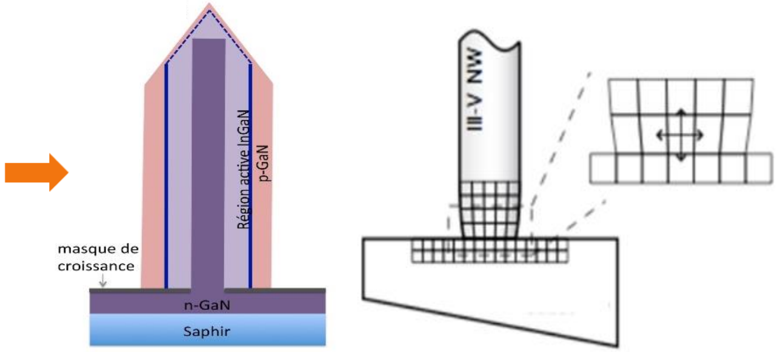
- Defect-free nano-objects on low-cost substrates
- Increase of the active surface – solution to the droop problem

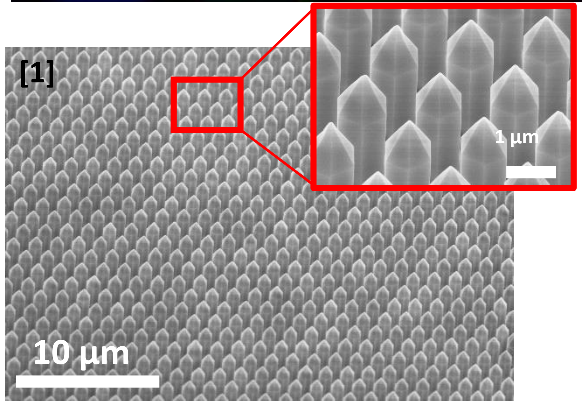
Standard architecture

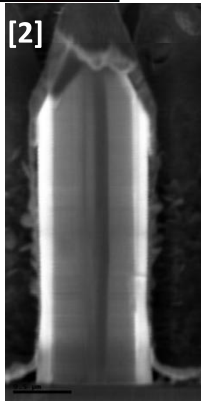




Nanowire architecture







Nanoscale analyses of energy efficiency in the LEDs

- Understand the operation down to the nanoscale
- Identify the problems
- Optimize the performance

[1] Tchernycheva M, Lavenus P, Zhang H, Babichev A V, Jacopin G, Shahmohammadi M, Julien F H, Ciechonski R, Vescovi G, Kryliouk O, InGaN/GaN Core/Shell Single Nanowire Light Emitting Diodes with Graphene-Based P-Contact, Nano Letters 14, 2456 (2014).

[2] Tchernycheva M, Neplokh V, Zhang H, Lavenus P, Rigutti L, Bayle F, Julien FH, Babichev A, Jacopin G, Largeau L, Ciechonski R, Vescovi G, Kryliouk O Core-shell InGaN/GaN nanowire light emitting diodes analyzed by electron beam induced current microscopy and cathodoluminescence mapping, Nanoscale 7, 11692 – 11701 (2015).

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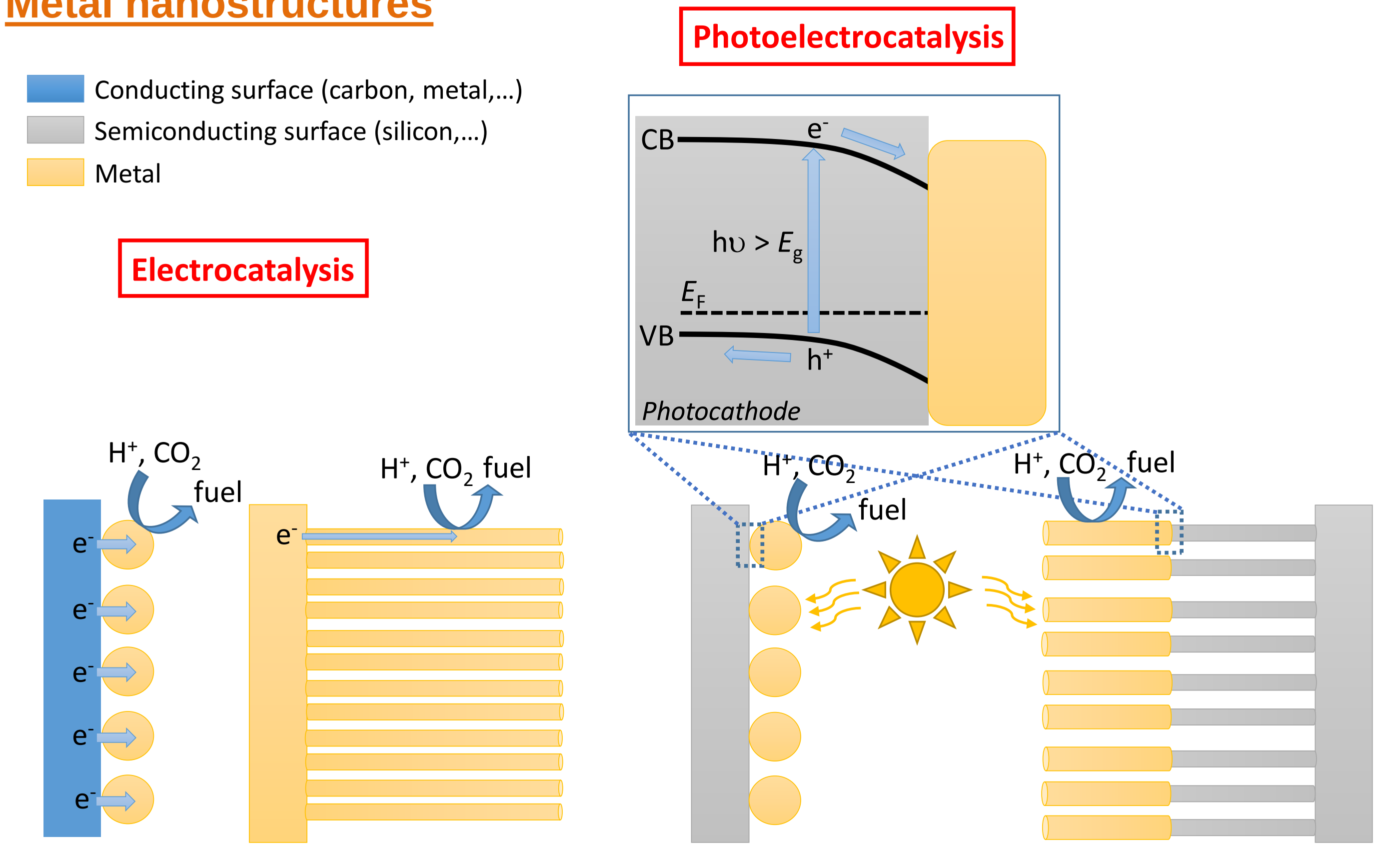
Metal nanostructures



Performance metrics:

- Current density (> 10 mA cm^{-2})
- Overvoltage for electrochemical water splitting and CO_2 reduction (vs archetypical Pt)
- Electrochemical stability (> several days)
- Selectivity, Faradaic efficiency, solar-to-fuel (H_2) efficiency

Conversion of Electric Energy to Chemical Energy

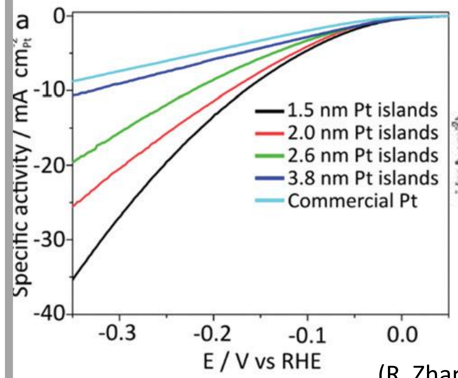
Metal nanostructures B. Fabre

Electrocatalysts for Hydrogen Evolution Reaction (HER)

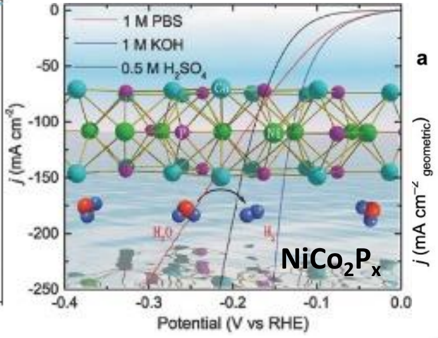
Noble metals

Non-noble metals
Ni > Mo > Co > W > Fe > Cu

Metal carbides, phosphides, nitrides and sulfides (TMDs)

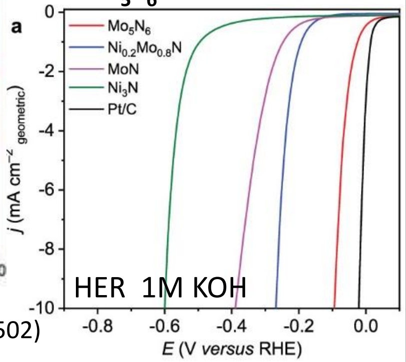


(R. D. Tilley, and co. *Chem. Commun*. **2021**, doi.org/10.1039/D0CC07769K)



(R. Zhang, et al. *Adv. Mater.* **2017**, *29*, 1605502)

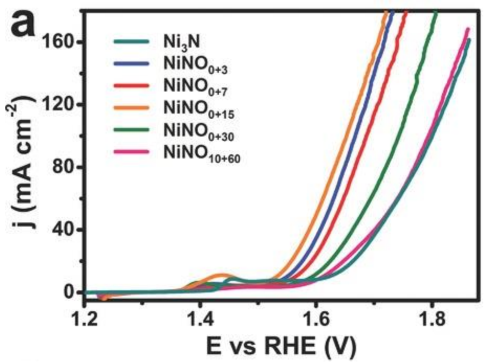
Mo$_5$S$_6$ Nanosheets



(H. Jin, et al. *ACS Nano* **2018**, *12*, 12761)

Electrocatalysts for Oxygen Evolution Reaction (OER)

Co- and Ni-based

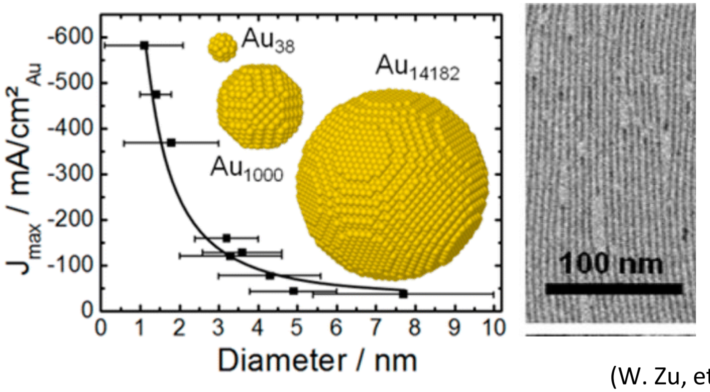


(J. Huang, et al. *Adv. Mater.* **2018**, *30*, 1803367)

Electrocatalysts for Carbon Dioxide Reduction Reaction (CDRR)

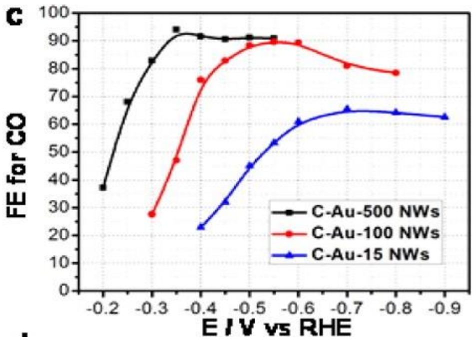
$CO_2 \rightarrow CO$

Au Nanoparticles



(H. Mistry, et al. *J. Am. Chem. Soc*. **2014**, *136*, 16473)

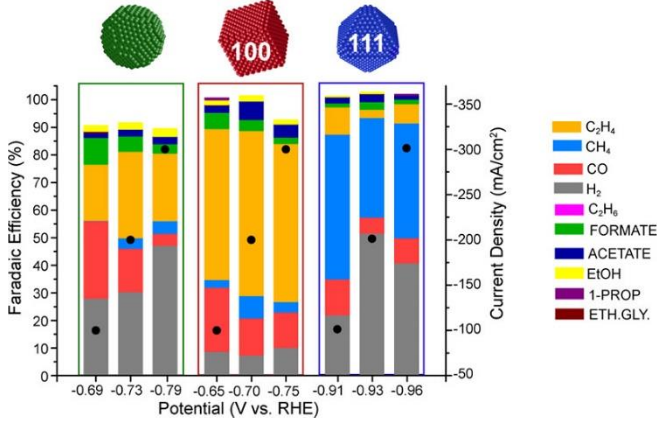
Au Nanowires



(W. Zu, et al. *J. Am. Chem. Soc*. **2014**, *136*, 16132)

$CO_2 \rightarrow$ Hydrocarbons

Cu Nanocrystals: structure-dependent selectivity



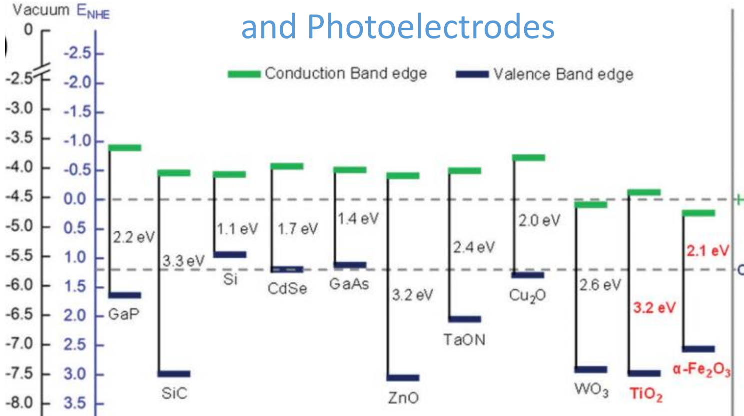
(G. L. De Gregorio, et al. *ACS Cat*. **2020**, *10*, 4804)

Conversion of Light Energy to Chemical Energy

Metal nanostructures

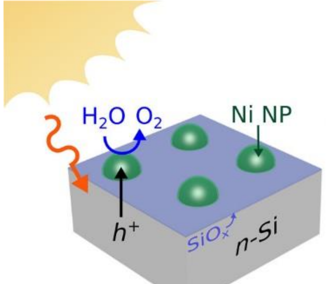
<u>Benefits of micro/nanostructures:</u> *better photon absorption,enhanced charge separation, large surface area and mass transport control*

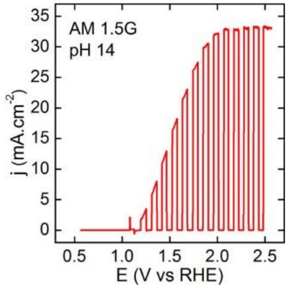
Nanostructured Photoelectrocatalysts and Photoelectrodes



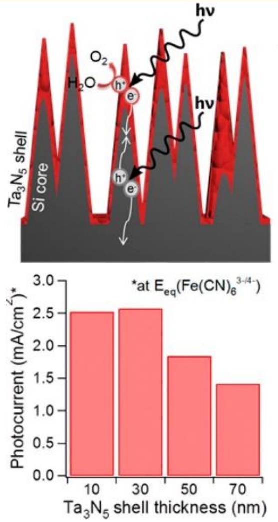
(From *Chem. Soc. Rev*. **2017**, *46*, 3716)

Photoanodes for OER



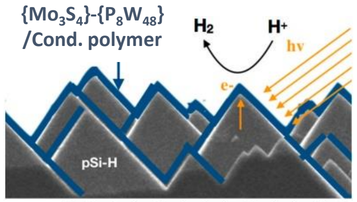


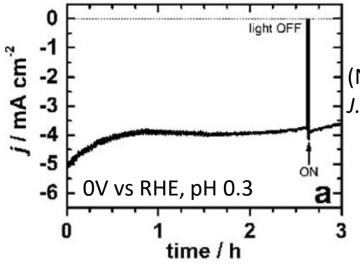
(G. Loget, et al. *ACS Energy Lett.* **2017**, *2*, 569;
S. W. Boettcher, *Nat. Mater*. **2020**, *19*, 69)



(T. F. Jaramillo, and co. *Nano Lett.* **2016**, *16*, 7565)

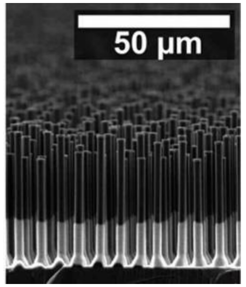
Photocathodes for HER





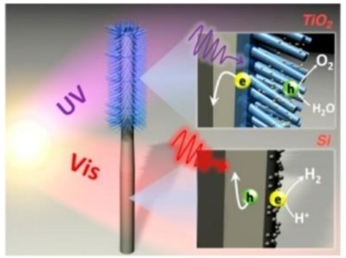
(B. Fabre, and co. *J. Am. Chem. Soc.* **2019**, *141*, 11954)

Pt/n$^+$p-Si wire-array



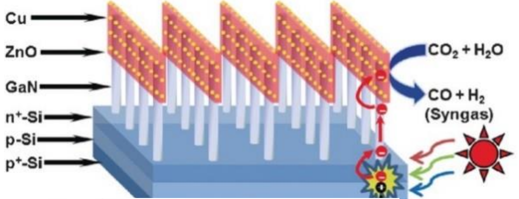
(N. S. Lewis, and co.
J. Am. Chem. Soc. **2011**, *133*, 1216)

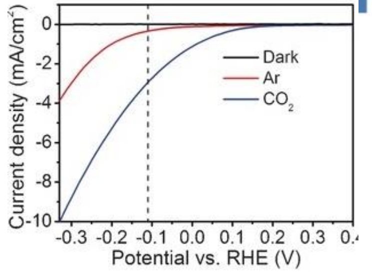
Mo_3S_4/p-Si wire-array
I. Chorkendorff,
Nat. Mater. **2011**, *10*, 434



(P. Yang, and co.
Nano. Lett. **2013**, *13*, 2989)

$CO_2 \rightarrow CO$



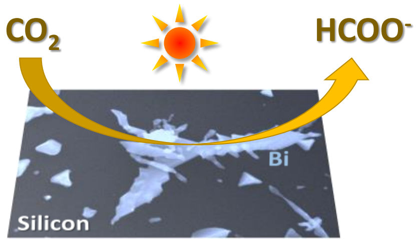


(S. Chu, et al. *Angew. Chem. Int. Ed.* **2016**, *55*, 14262)

Photocathodes for CDRR

$CO_2 \rightarrow HCOO^-$

Bi-modified p-Si



pH~7, 24 mA cm^{-2} at -1.0 V vs RHE,
Selectivity > 72%

(B. Fabre and co., *ChemCatChem* **2020**, *12*, 5819)

Trends and Prospects

(Photo)electrochemical water splitting:

- Performance of metals-based catalysts > molecular catalysts (current density, overvoltage and electrolytic stability)
- Great promises for metal carbides, phosphides, nitrides and sulfides
- Scalable technology based on Earth-abundant materials and cost-effective preparation, deposition manufacturing processes

CO_2 reduction:

- Metal nature and structure-dependent selectivity (CO, HCOOH, hydrocarbons)
- Competition between H_2 production and formation of C products
- High current densities for gas diffusion electrodes
  (a step towards viable CO_2 valorization)

Electrodes vs Photoelectrodes:

- Activation of the electrochemical process for photoelectrodes (due to photovoltage)
- Limited solar-to-hydrogen efficiency for photoelectrodes: photocorrosion issue under alkaline conditions
- Use of non-conventional semiconductors (e.g. III-V SCs)

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6. General conclusions & perspectives

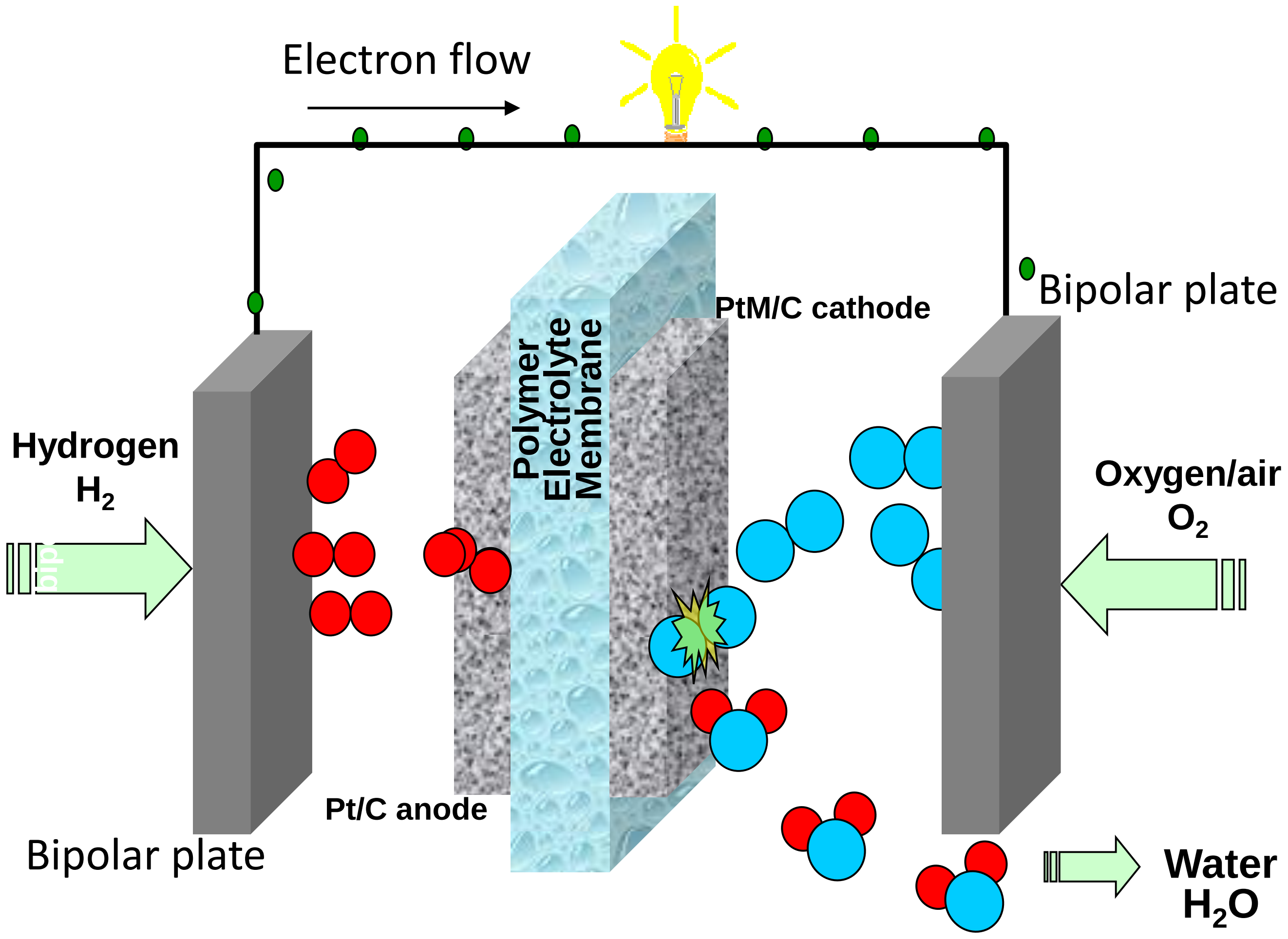
The French Research network on Hydrogen energy

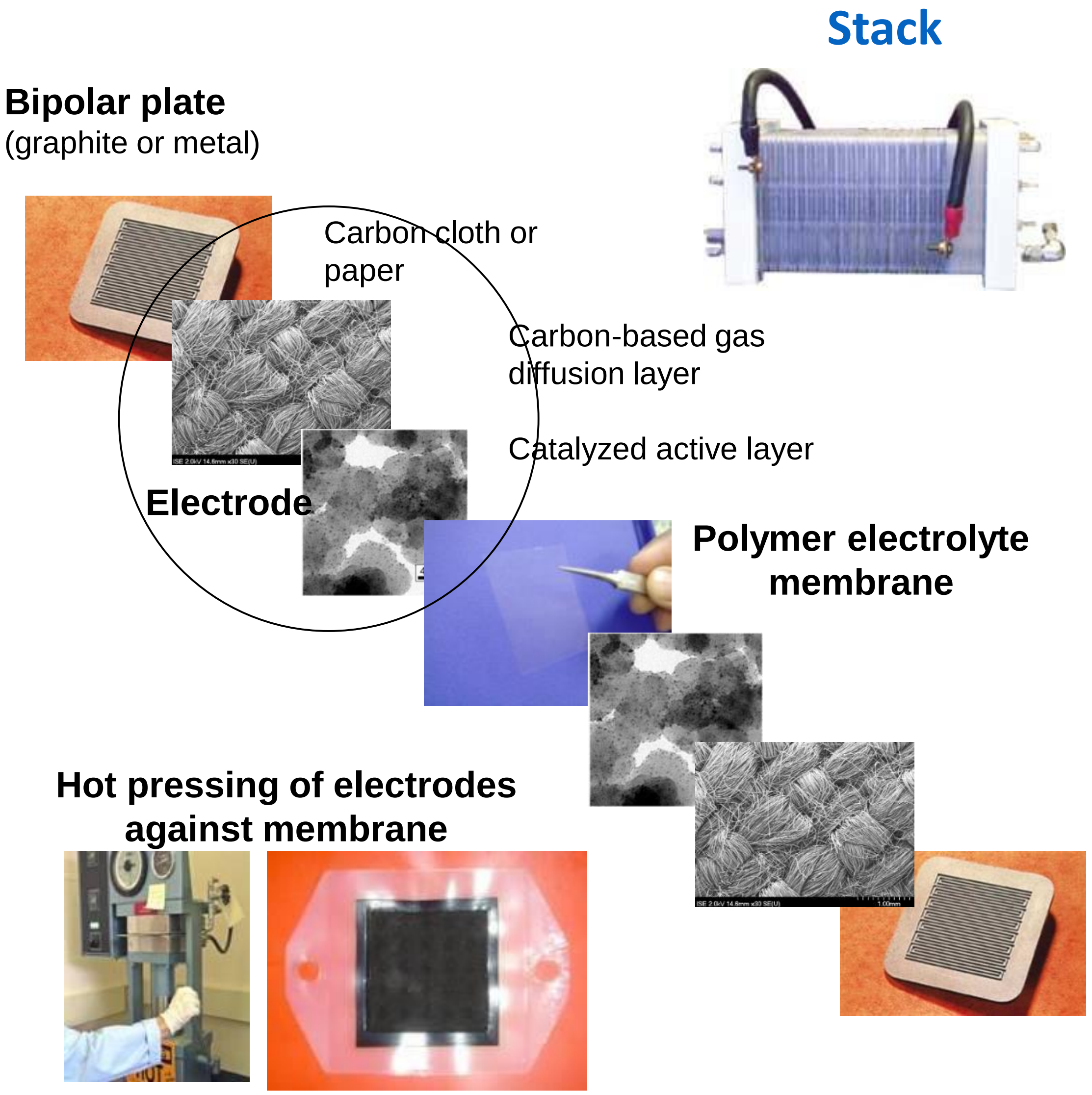
Christophe Coutanceau, Marian Chatenet

Proton Exchange Membrane Fuel Cells (PEMFCs)

Working Group 3 : Energy Conversion

Working principle of a Proton Exchange Membrane Fuel Cell





C. Lamy, D. Jones, C. Coutanceau, P. Brault, S. Martemianov, Y. Bultel. Do not forget the characteristics of the Membrane-Electrode-Assembly when designing a PEMFC stack. Electrochim. Acta 56 (2011) 10406-10423.

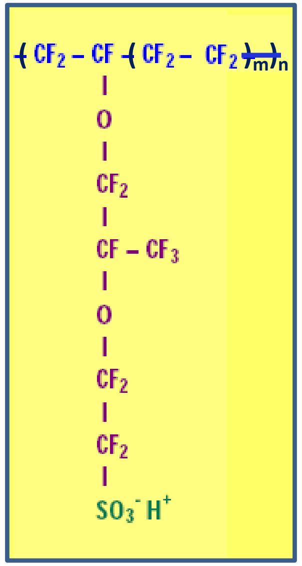
Cell core = Membrane-Electrodes Assembly (MEA)

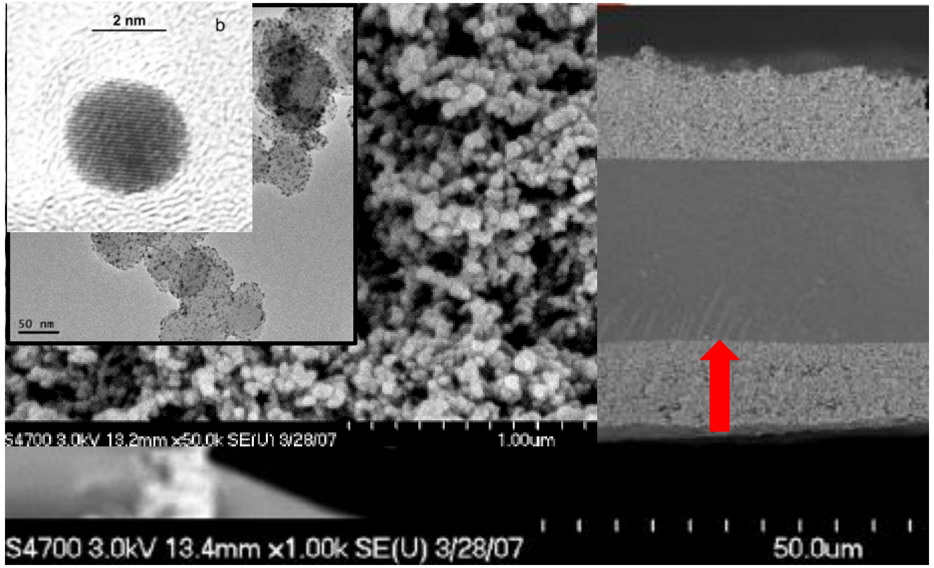
Working principle of a Proton Exchange Fuel Cell

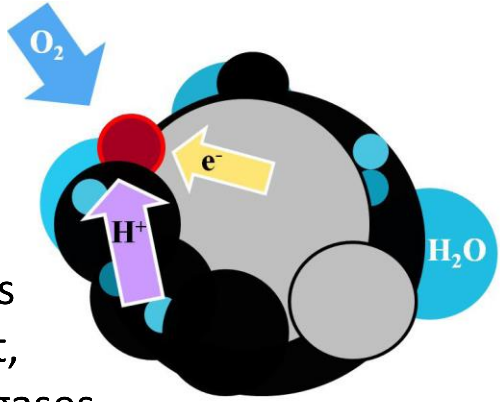
MEA / Electrodes

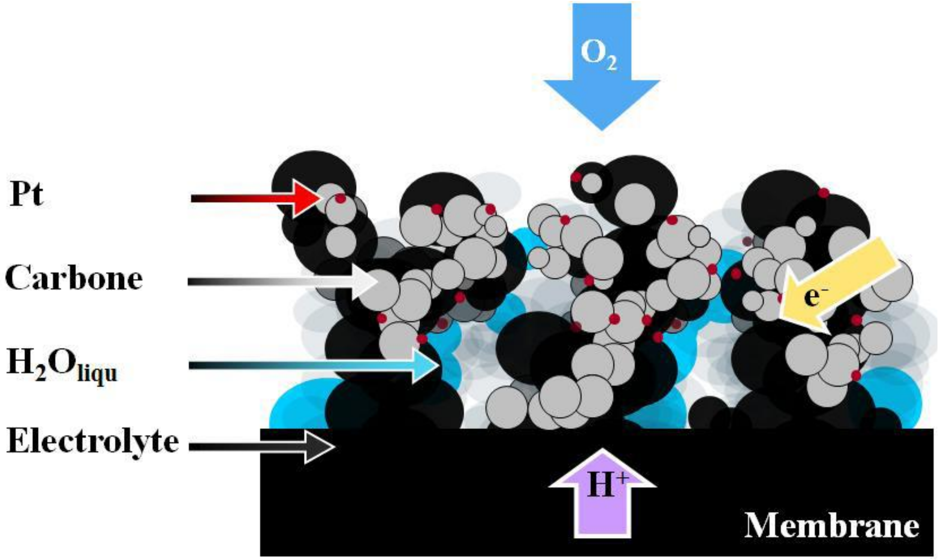
Nafion® (Du Pont)

Protons Exchange Membrane



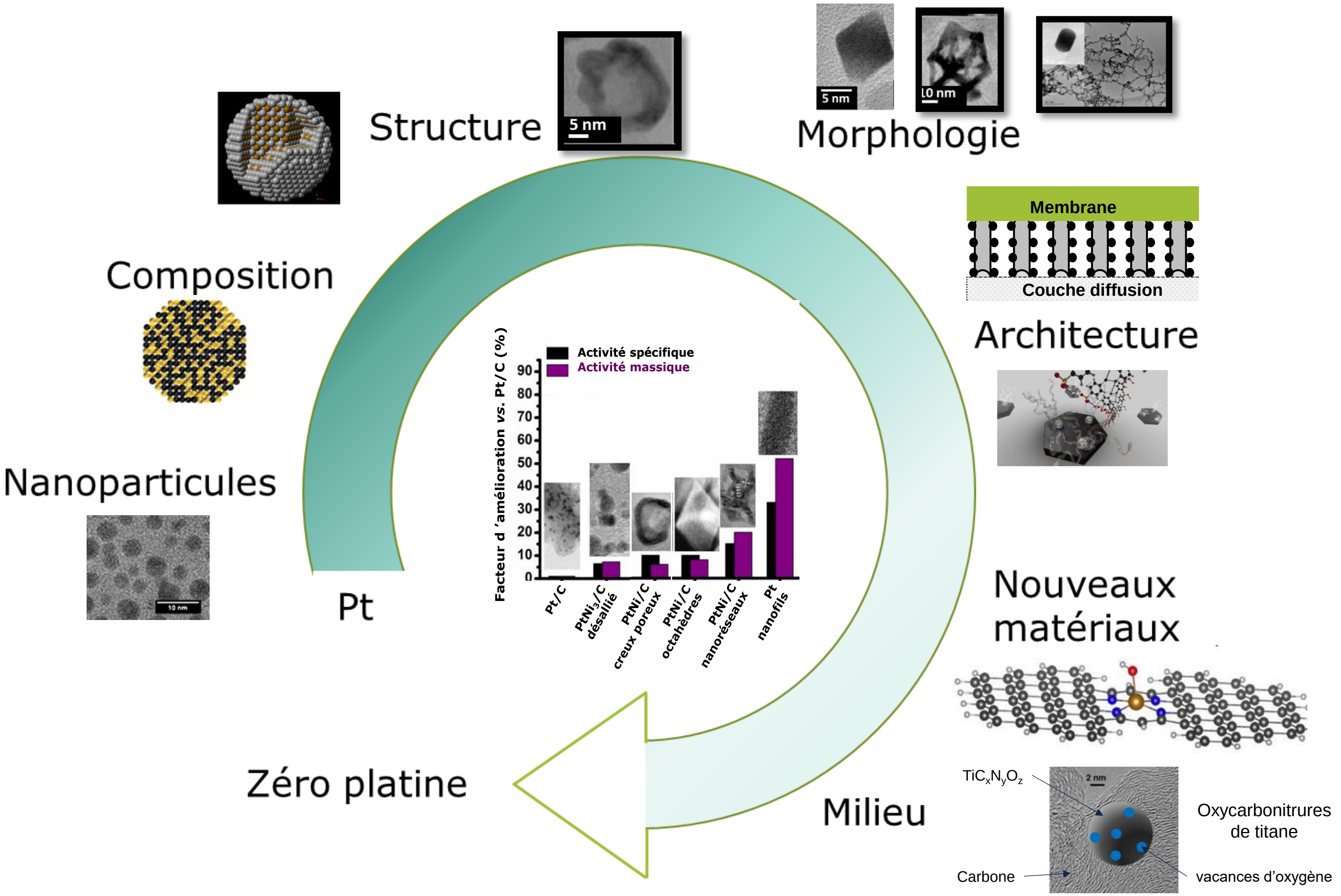






The reactions proceed at triple phase-boundaries between the carbon-supported Pt-based catalyst, the ionomer and the pores feeding the reactive gases

Strategy to decrease platinum content and increase performances and durability



Actors of FR H2 2044 CNRS :

LEPMI Grenoble - Chambéry

ICGM Institut Charles Gerhardt Montpellier

ICPEES Institut de Chimie et Procédés pour l'Énergie, l'Environnement et la Santé

GREMI

IC2MP Institut de Chimie des Milieux et Matériaux de Poitiers

R. Chattot, V. Beermann, S. Kühl, J. Herranz, S. Henning, L. Kühn, T. Asset, L. Guétaz, O. Le Bacq, G. Renou, J. Drnec, P. Bordet, A. Pasturel, A. Eychmüller, T. J. Schmidt, P. Strasser, L. Dubau, F. Maillard, *Nat. Mater*. **17** (2018) 827

A. Zalineeva, S. Baranton, C. Coutanceau, G. Jerkiewicz, *Sci. Adv.* 3 (2017): e1600542; D. Dru, S. Baranton, J. Bigarré, P. Buvat, C. Coutanceau, ACS Catalysis 6 (2016) 6993

P. Brault, C. Coutanceau, A. Caillard, S. Baranton, J. Phys. Chem. C 123 (2019) 29656

T. Mineva, I. Matanovic, P. Atanassov, MT Sougrati, L. Stievano, M Clémancey, A. Kochem, J-M. Latour, F. Jaouen, *ACS Catalysis* 9 (2019) 9359;

J. Li, M-T. Sougrati, A. Zitolo, J.M. Ablett, I.C. Oguz, T. Mineva, I. Matanovic, P. Atanassov, A. Di Cicco, K. Kumar, L. Dubau, F. Maillard, F. Jaouen, Nature Catalysis 4 (2021) 1019

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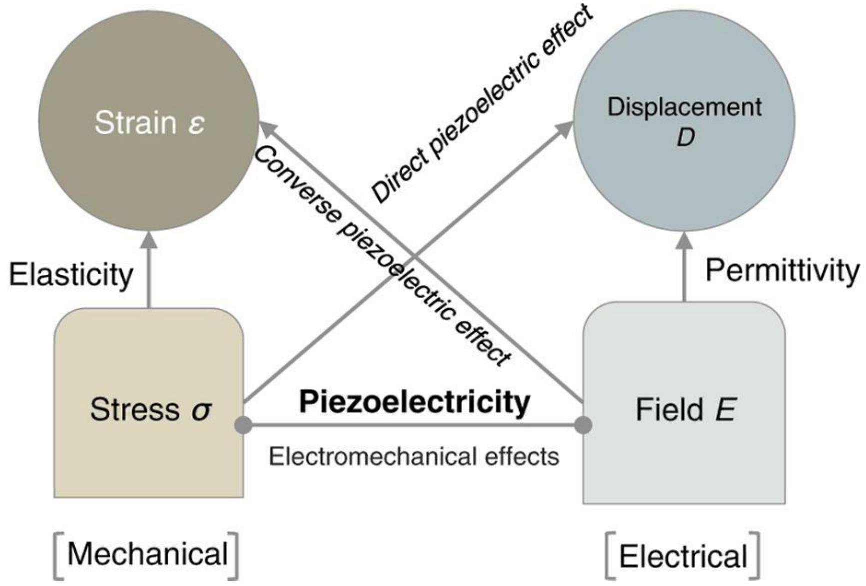
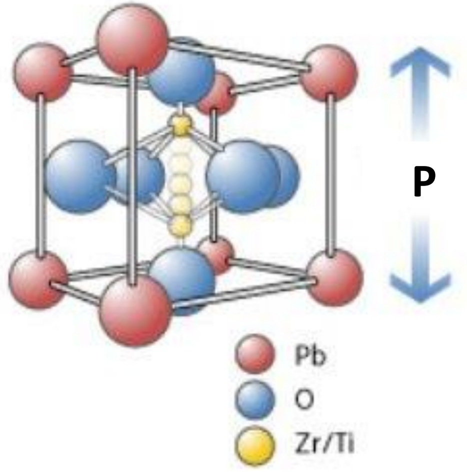
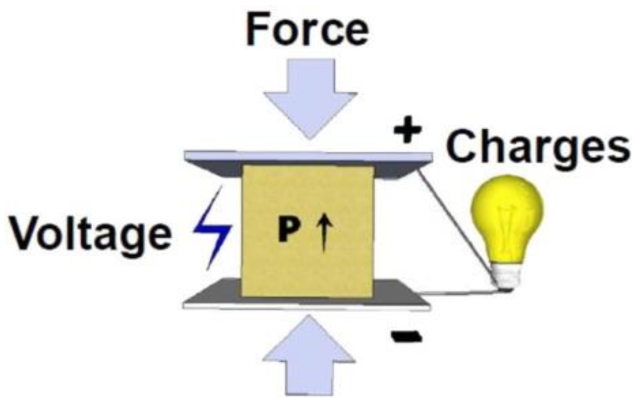
Piezoelectricity

<u>Principle</u>: electricity resulting from pressure and vice-versa



Part of the Heckman Diagram, Jong et al., Sci. data (2015)
doi:10.1038/sdata.2015.53



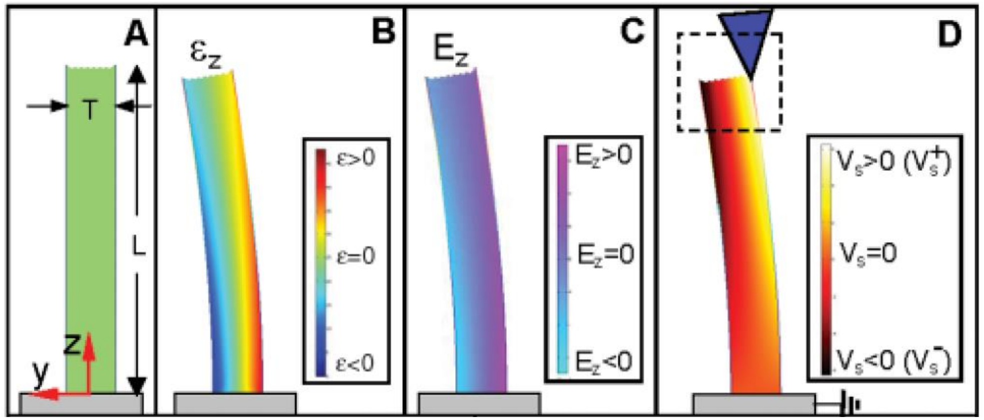


$d_{ij} = dP / d\sigma$ (C/N)

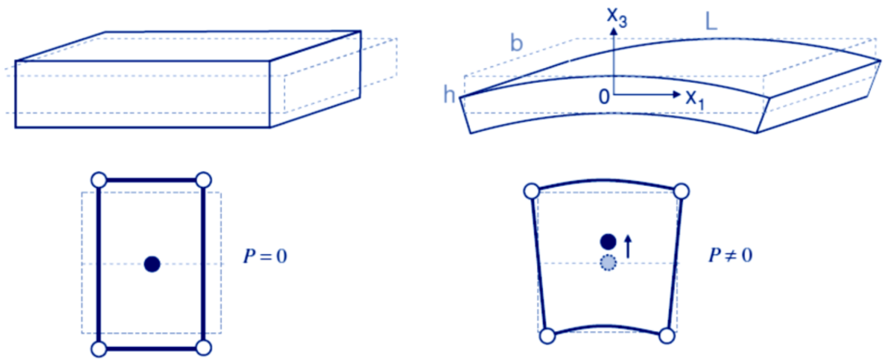
FoM = d_{ij}^2 / ε

Piezoelectric NWs for nanogenerators

The applied stress results in a piezoelectric field along the length or diameter, which causes a transient charge flow in the external circuit.



Z. L. Wang et al. Science (2006)
doi:10.1126/science.1124005



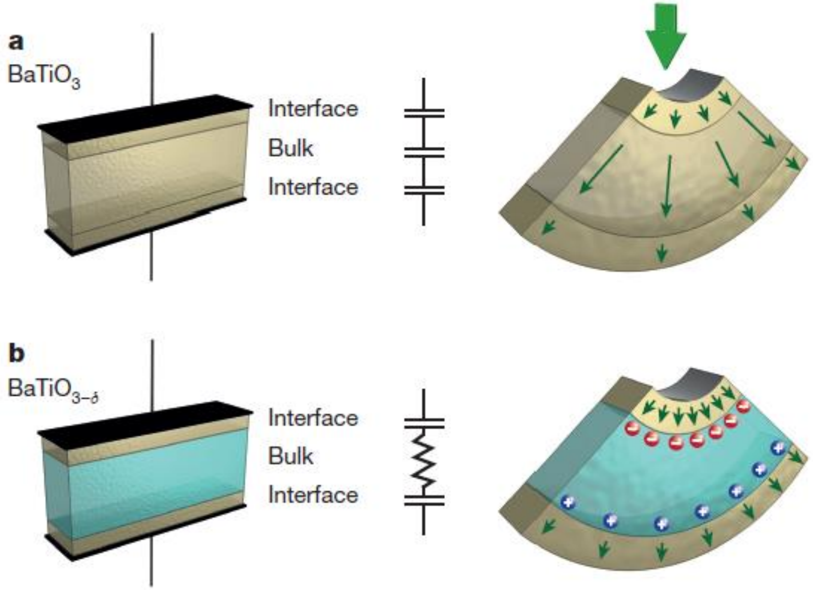
Flexoelectricity

Strain-gradient induced electric polarization in a dielectric material

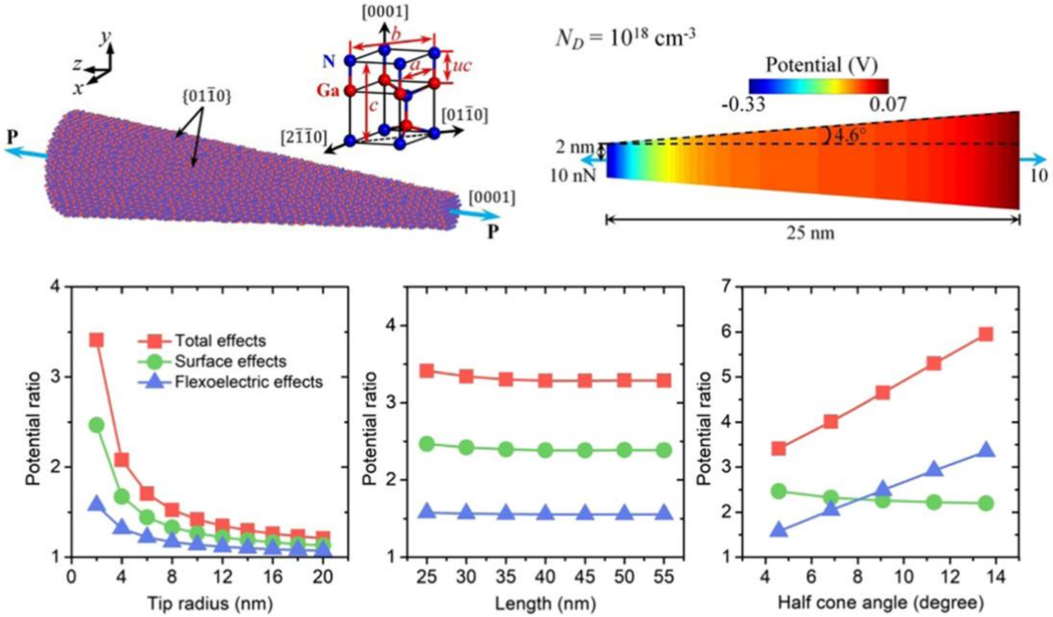
In single-crystals, thin films, membranes, nanowires…

P. Zubko et al., An. Rev. Mater. Res. (2013)
doi: 10.1146/annurev-matsci-071312-121634

Enhanced in oxide semiconductors



J. Narvaez et al., Nature (2016)
doi:10.1038/nature19761



Present in 1D-nanostructures

J. Zhang et al. Nano Energy (2021)
doi: 10.1016/j.nanoen.2020.105489

Piezoelectric nanogenerators

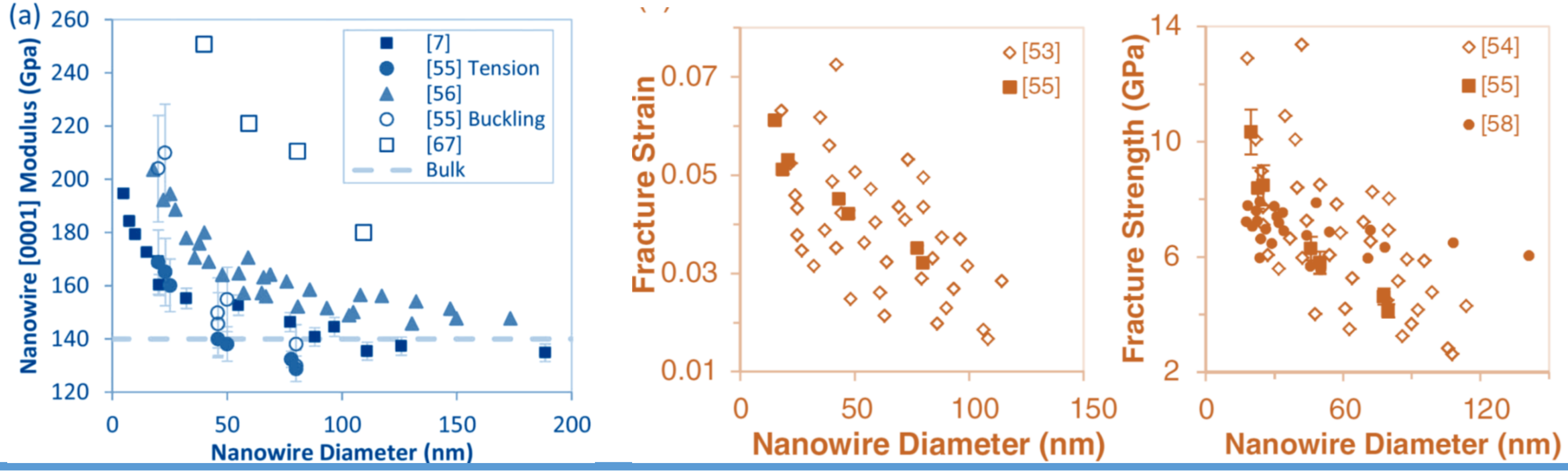
Influence of nanomaterials

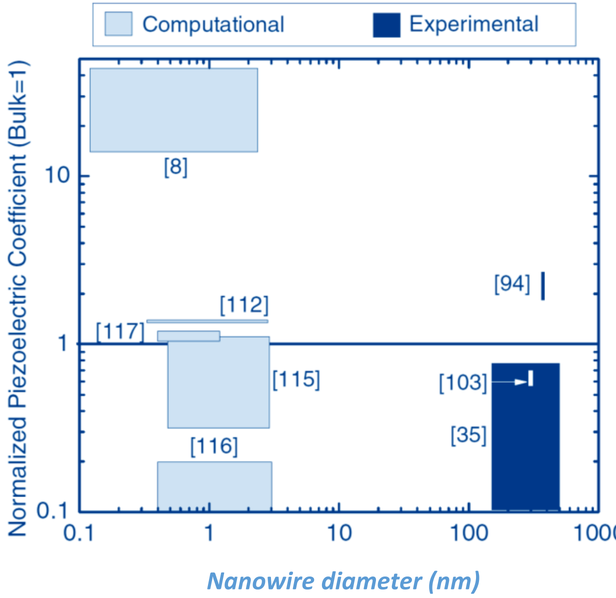
No figure of merit, but *enhanced performance compared to bulk or film systems*

enhanced properties for NW below 10 nm/100 nm diameter (*theory*/ *experience*)

- Higher mechanical properties: *Young modulus, fracture strength*
- Higher sensitivity to deformation without plastic damages
- Exhalted piezoelectric coefficients:

Experimental / Review: H. D. Espinosa et al., Adv. Mater. 24 (2012) 4656-4675





Values normalized with bulk ones

Piezoelectric nanogenerators

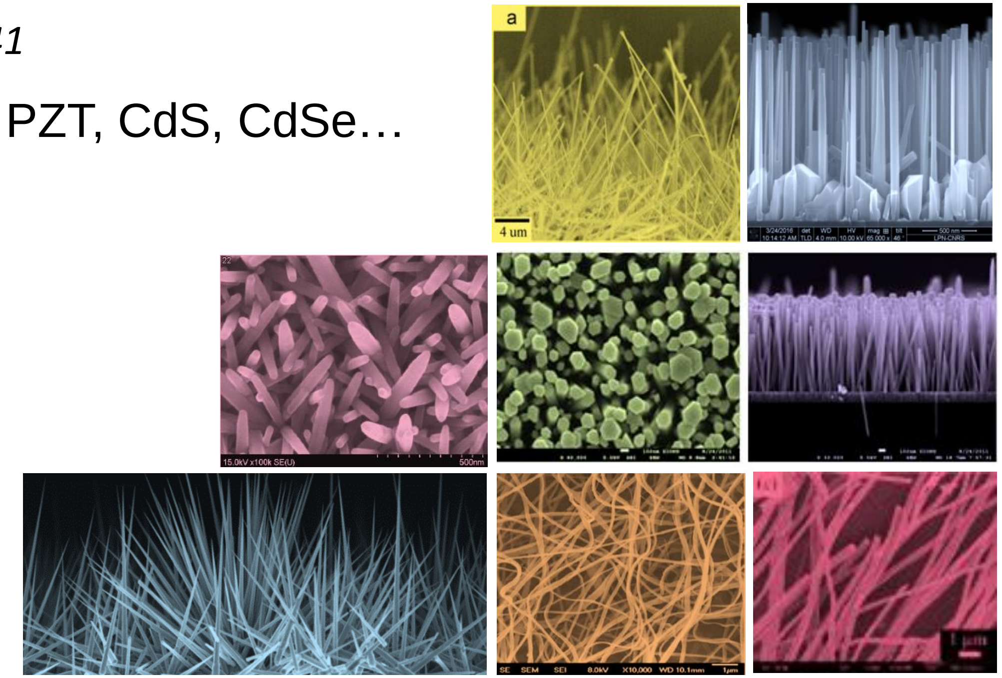
Last trends

✓ Large literature on ZnO nanowires /nanorods grown by **chemical or physical methods**

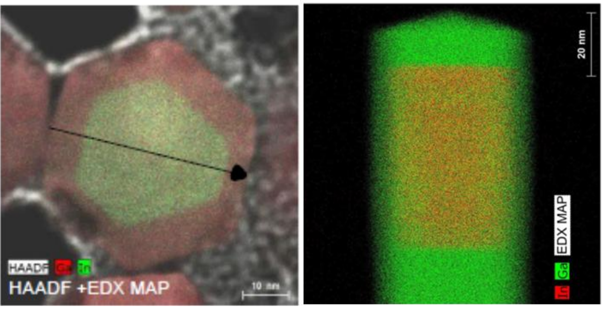
H. D. Espinosa et al., Adv. Mater. 24 (2012) 4656-4675
A. J. L. Garcia, M. Mouis, V. Consonni, G. Ardila, Nanomaterials, 11(4) (2021) 941

✓ Other piezo materials with various synthesis methods: GaN, PZT, CdS, CdSe…

R. Hinchet et al., In IEEE 2012 Int. Electron Devices Meeting, 6.2.1-6.2.4
E. L. Perez, PhD Univ. Grenoble Alpes (2016)



Matériau	Matériau massif (expérimental)		Echelle nanoscopique (expérimental)	
	d_{33} (10^{-12} m/V)	E (GPa)	d_{33} (10^{-12} m/V)	E (GPa)
ZnO	9.93	164	14-26.7	100
GaN	1.86	397	12.8	43.9
PZT	650	N/A	101	46.4-99.3
PVDF	-25	N/A	-38	0.39



✓ Heterostructured NWs

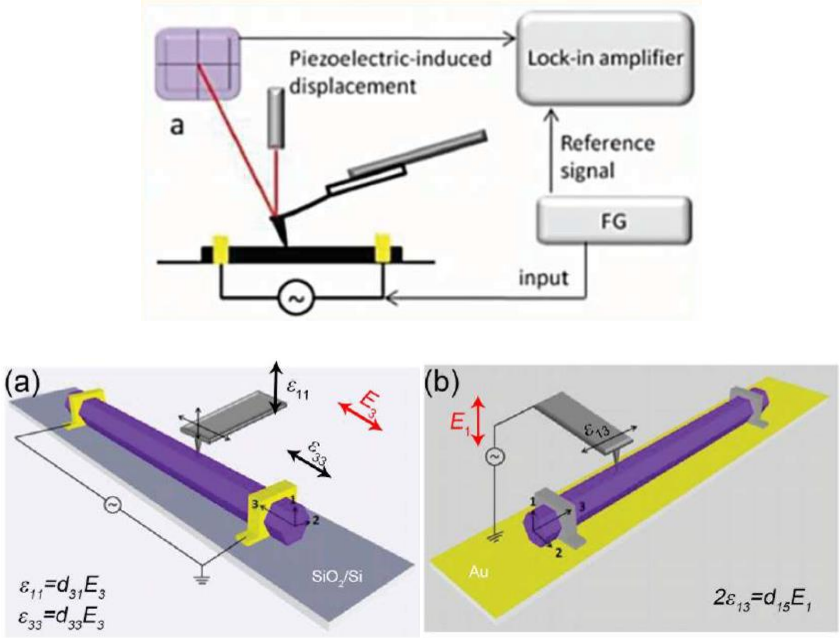
The piezo-conversion of InGaN/GaN NWs is 30% more efficient than GaN

N. Jegenyes et al., Nanomaterials 8(6) (2018) 367, doi: 10.3390/nano8060367

Piezoelectric nanogenerators

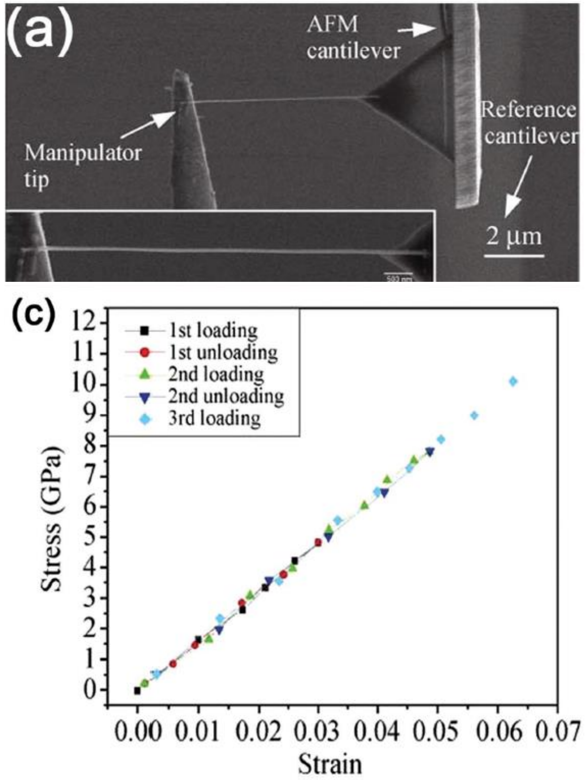
Last trends Experimental evaluation of electrical & mechanical properties of NWs : **dedicated methods**

Piezoelectric coefficients



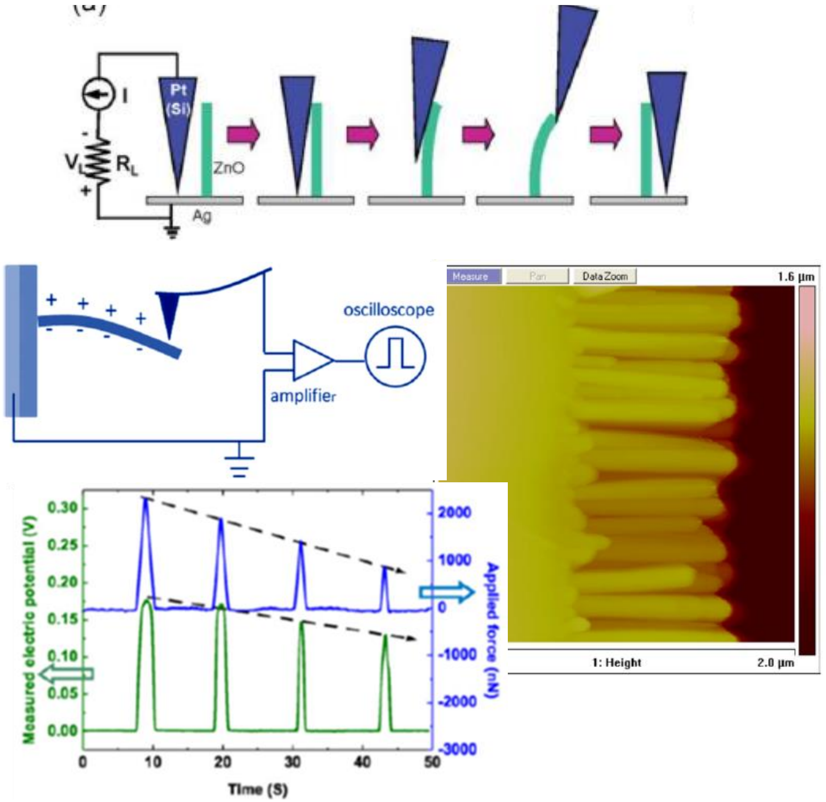
M. Minary-Jolandan et al., NanoLett. 12 (2012) 970

Mechanical properties



S. Wang et al., Adv. Science 4, 4 (2017) 1600332

Piezoelectric conversion properties



Z.L. Wang, Science 2006; X. Xu et al. , Nanotechnology 22 (2011) 105704 (8pp)

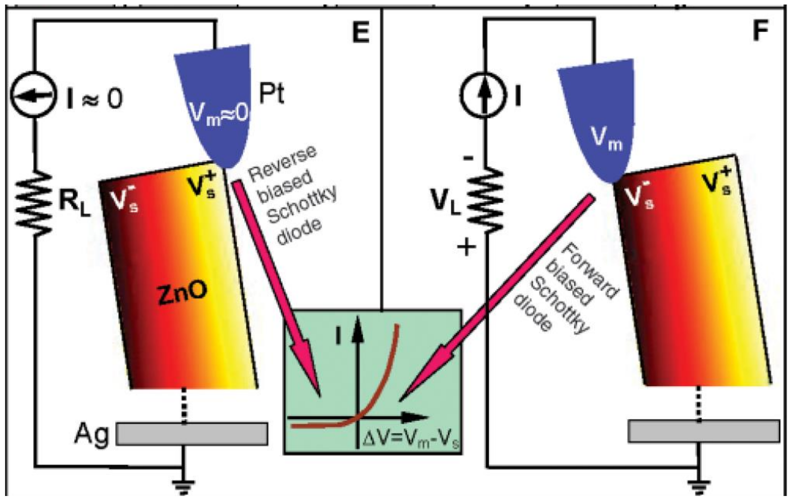
Piezoelectric nanogenerators

Electromechanical conversion properties measurement

AFM with electrical module: The main used technique to characterized NW-based nanogenerators!

Based on Schottky diode which regulates the charge flow

⇒ NW bending/releasing creates an alternating flow of charges in the external circuit.



Z. L. Wang et al. Science (2006)
doi:10.1126/science.1124005

Schottky diode influenced by material characteristics

- Semiconductor material polarity
- Type of doping
- Applied deformation

Schottky diode influence the energy harvesting efficiency

Nano-contact effects

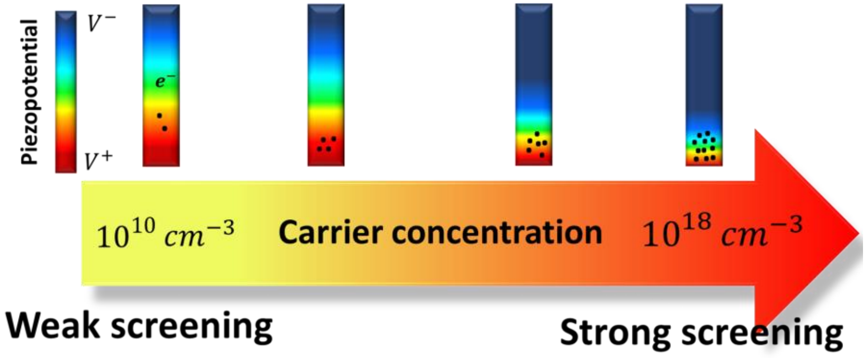
N. Gogneau et al. Semicond. Sci. Technol. 31 (2016) 103002, ***doi:10.1088/0268-1242/31/10/103002***
N. Jamond et al., Nanoscale, 9 (2017) 4610-4619, ***doi: 10.1039/C7NR00647K***

Piezoelectric nanogenerators

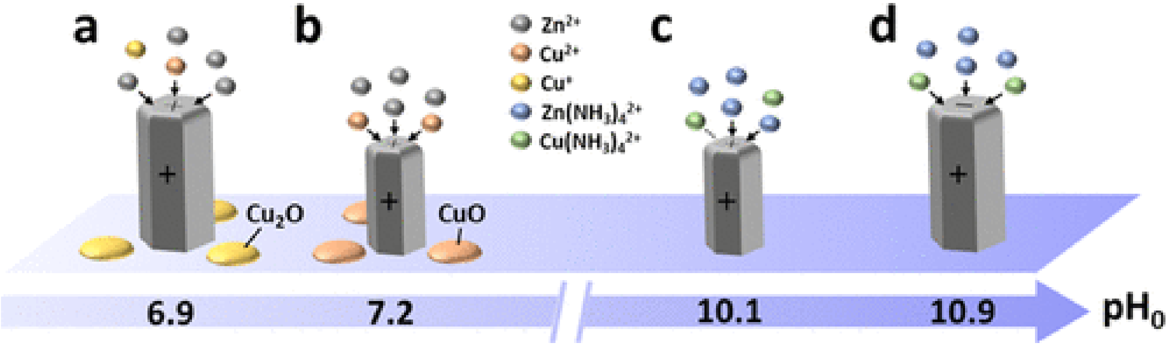
Last trends: doping of NWs

Intrinsic doping of NW [1,2] + Intentional doping for further enhancement of piezoelectric conversion properties [3,4]

[1] S. Boubenia, Thèse Univ. Tours, 2019, hal.archives-ouvertes.fr/tel-02975514
[2] J. Villafuerte et al. The Journal of Physical Chemistry C 124, 16652-16662 (2020)
[3] X. Li et al., Nanomaterials 2018, 8, 188, doi:10.3390/nano8040188
[4] S. Goel, B. Kumar, J. of Alloys and Compounds 816 (2020) 152491



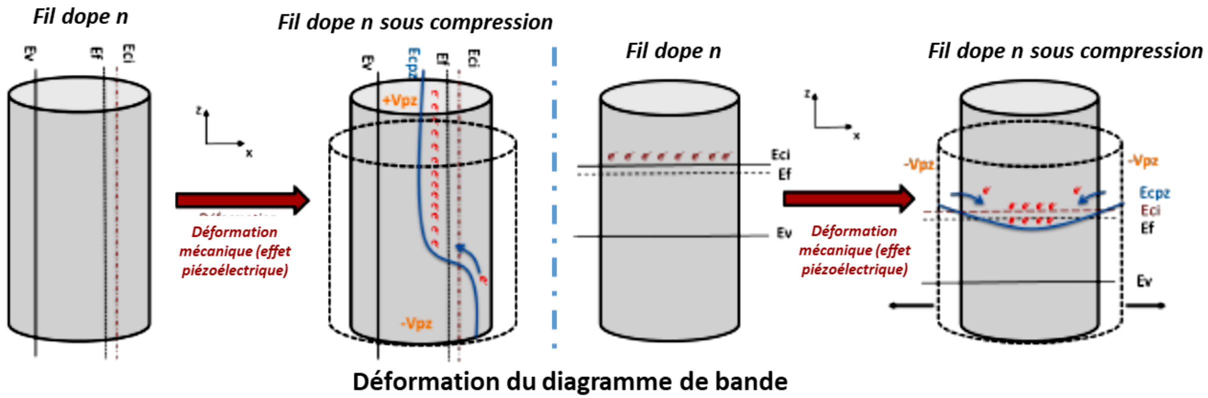
In ZnO: the high free electron density coming mainly from hydrogen should be decreased.



Compensating doping with Cu to decrease the free electron density in ZnO NWs grown by chemical bath deposition

C. Lausecker et al. Inorganic Chemistry 60, 1612-1623 (2021)

In GaN: Role of the dopant, extrinsic doping.

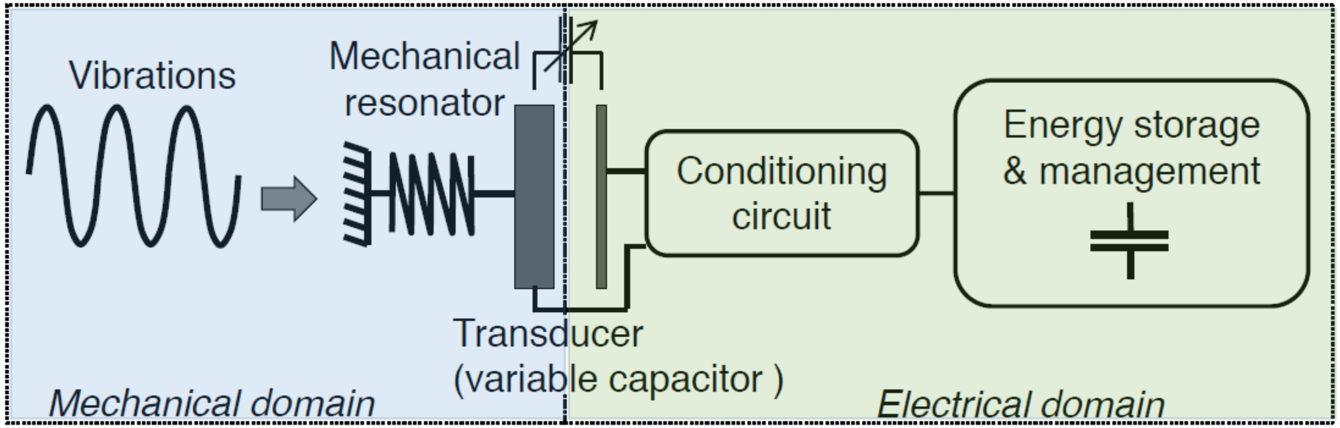


A. El Kacimi, PhD Grenoble Alpes (2017)

Philippe Basset

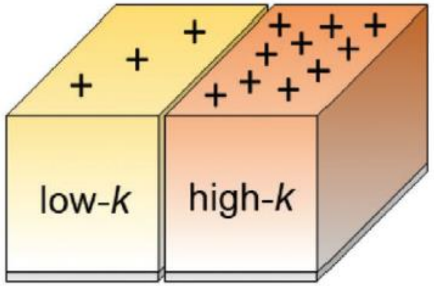
Electrostatic Kinetic Energy Harvesters (e-KEH)

Principle:



[P. Basset, E. Blokhina, D. Galayko, ISTE-Wiley, 2016]

- A biased-capacitor varies because of an external mechanical force
  - → The negative work of the electrostatic force acting on the mobile electrode = to the mechanical-to-electrical converted energy
- The converted energy is maximized with:
  - a high capacitance variation of the electrostatic transducer (C_{max}/C_{min})
  - a high bias voltage
    - → electret with high-*K* material (ε)
    - → electret with high surface-charge density (σ)

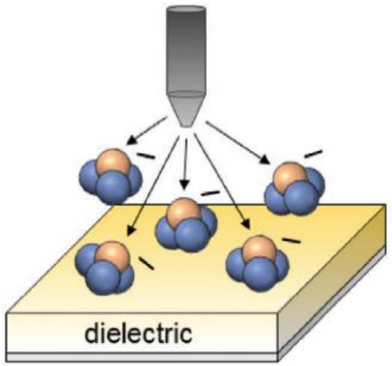


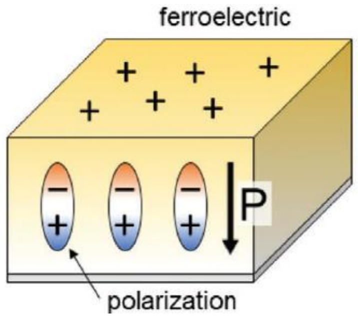
Philippe Basset

Electrostatic Kinetic Energy Harvesters (e-KEH)

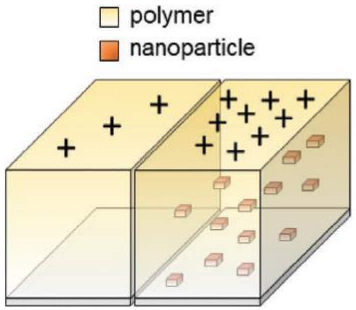
How to improve e-KEH at the material level?

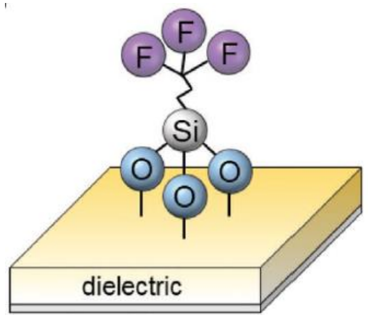
- During fabrication:
  - Injections of ions/electrons in the electret → σ++
    - Corona injection, soft X-ray, e-beam…
    - « Solid-state » electret, ferro-electret
  - Add of nanoparticles inside the electret
    → Improve permittivity → C_{max} ++
    → and/or charge storage and/or triboelectric affinity → σ++
  - Flexibility of dielectric material (soft polymer) → C_{max}/C_{min} ++
- « At work »: tribo-electrification →σ++
  → Nano/micro surface structuration of "tribo"-electret and contact electrode
  → Effect of self-assembly monolayer or 2D-material at the contact interface





[Y.S. Choi *et al*, *Adv. Energ. Mat.*, 2021]





Main performances : 1-100 µJ/cm²/mech. cycle @ a few *g* - kPa & a few tens of volts

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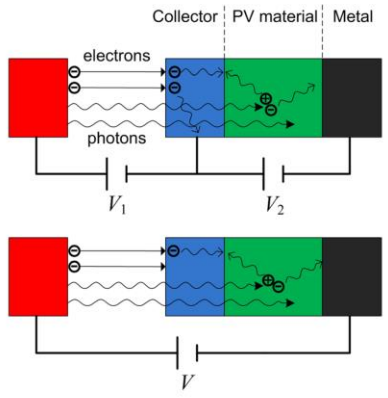
Hybrid – cogeneration: thermionic-thermophotovoltaic converter

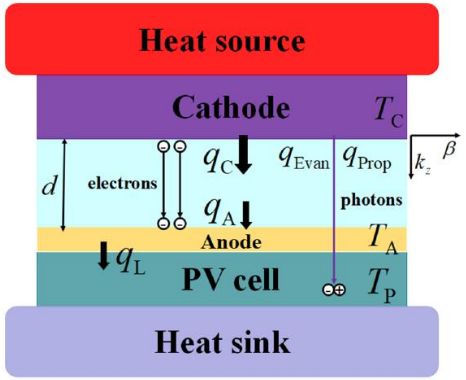
Rodolphe Vaillon

- Concept: proposed in 2016 (far field) and 2019 (near field)

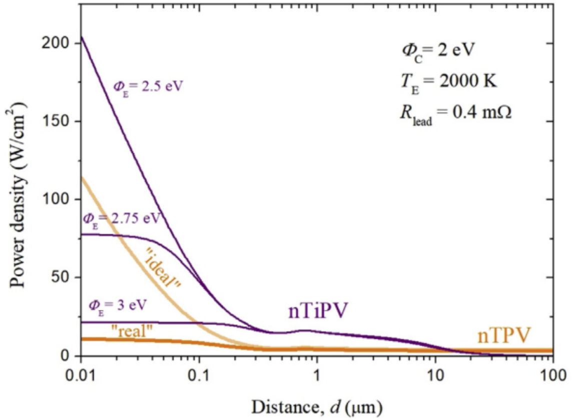
(Datas, Appl. Phys. Lett., 2016)

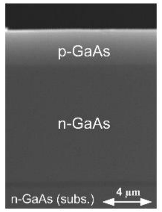


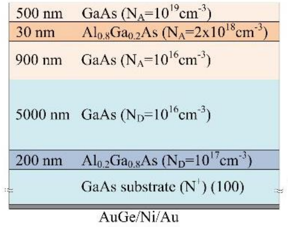
(Liao et al., J. Appl. Phys., 2019)

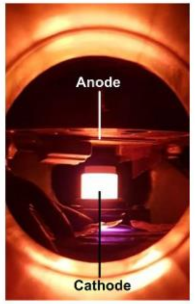


(Datas & Vaillon, Nano Energy, 2019)



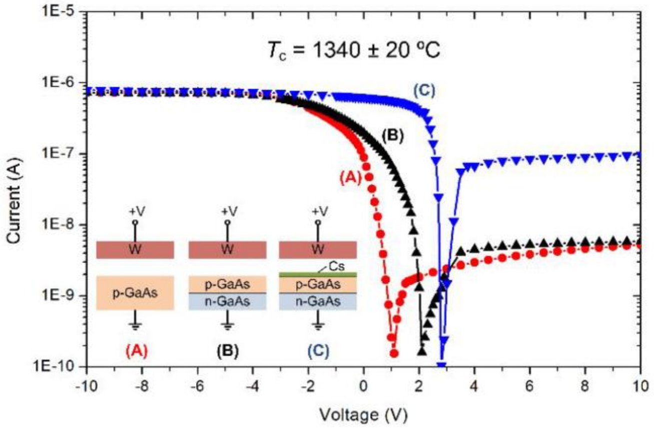






- Nanomaterials: requirements for both the thermionic and thermophotovoltaic effects. Spacers (for nanoscale gaps) blocking phonons and electrons

- Performances: (exp.) proof of concept (Bellucci et al., ACS Energy Lett. 5, 1354-70, 2020)
  (theo., near field): elec. power up to 70 W.cm^{-2} with efficiency ~30%



- Basic research
- Needs for the future: (nano-)materials and structures, experimental demonstration (near field)

1. Thermal ⇔ Electric

1.1. Pyroelectricity et (electro)caloric effect (*Romain Bachelet*)
1.2. Thermoelectricity (*Nicolas Stein*)
1.3. Radiative thermoelectric & Thermo-photovoltaic (*Rodolphe Vaillon*)

2. Optical ⇔ Electric

2.1. Photovoltaic (*Andrea Cattoni*)
2.2. Light Emitting Diodes (*Maria Tchernycheva*)

3. Chemical ⇔ Electric

3.1. Photo-electrochemical (*Bruno Fabre*)
3.2. Fuel cells (*Christophe Coutanceau*)

4. Mechanical ⇔ Electric

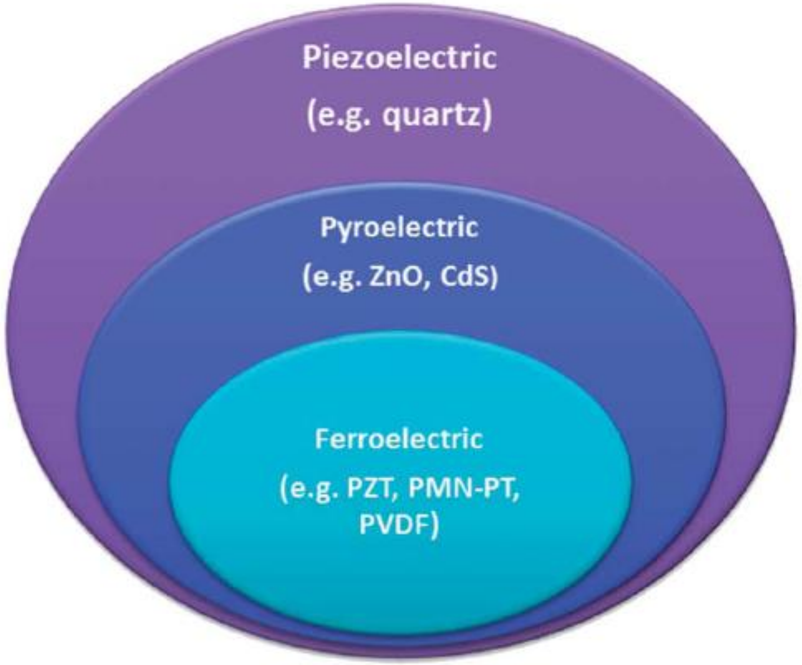
4.1. Piezo/flexo-electric (*Guylaine Poulin-Vittrant*)
4.2. Electrostatic (*Philippe Basset*)

5. Hybrides/multiples

5.1. Thermionic - TPV (*Rodolphe Vaillon*)
5.2. Piezo-pyro-tribo-photo-electric (*Romain Bachelet*)

6. General conclusions & perspectives

Piezo-pyro-tribo-photo-electric

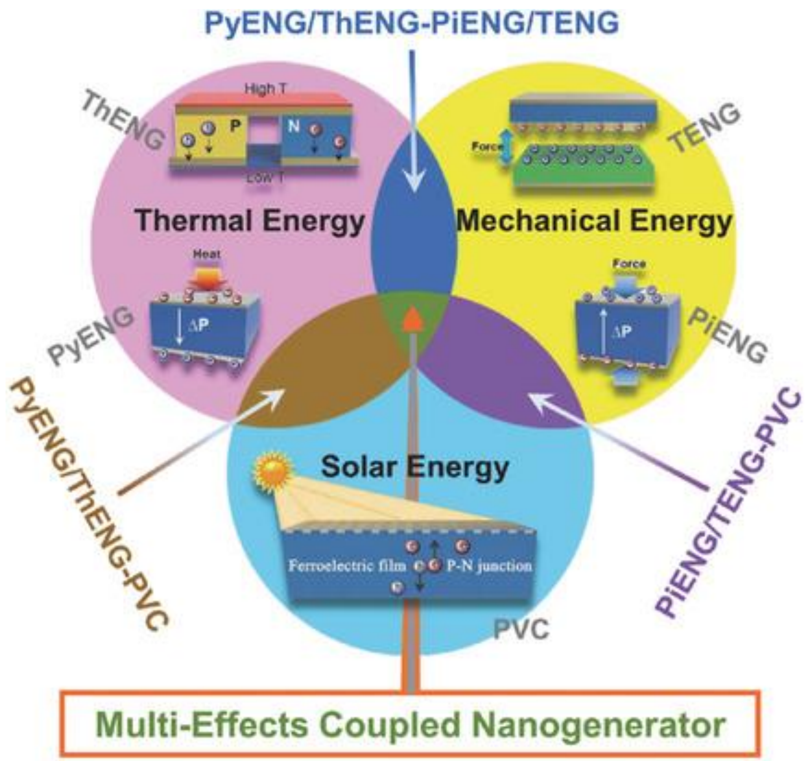


Piezo & Pyro-electric
(BaTiO3)
K. Song *et al.*, Adv. Mater. **(2019);**
https://doi.org/10.1002/adma.201902831

Piezo, pyro & tribo-electric!
(P(VDF-TrFE))
J. Kim *et al.*, Adv. Funct. Mater. **(2017);**
https://doi.org/10.1002/adfm.201700702

Other Hybrid/multiple conversions ?...

A One-Structure-Based Piezo-Tribo-Pyro-Photoelectric Effects Coupled Nanogenerator for Simultaneously Scavenging Mechanical, Thermal, and Solar Energies



K. Zhang *et al.*, Adv. En. Mater. **(2017);**
https://doi.org/10.1002/aenm.201601852

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6. General conclusions & perspectives

General conclusions and perspectives

- > 17 participants
- Highly multidisciplinary!
- Not exhaustive – could be extended!...
- More details & prospects in the next October plenaries ?
- Links with the other workgroups
- Chapter in the coming White paper
- Quantification of the conversions: towards normalization/standardization ?
  ➔ dedicated workshop ? Round Robin ?...

Thanks to the participants in the workshop!

Questions ?

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Thanks to all the participants in this Workshop!

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