TUNABILITY OF PHYSICAL-CHEMICAL PROPERTIES IN NANO-SYSTEMS

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UNESCO-UNISA Africa Chair in Nanosciences/Nanotechnology (South Africa)

PRESENTER BIO

- PhD in Wave Matter Neutron Optics 1993
- Joint staff iThembaLABS-NRF & UNISA
- UNESCO UNISA ITLABS-NRF Africa Chair in Nanosciences & Nanotech
- Research interest: Nanoscale
- Fellow of the African Academy of Sciences
- Fellow of the Royal Society of Chemistry-London
- Fellow of the National Academy of Sciences of India
- Fellow of the New York Academy of Sciences
- Fellow of the Islamic Academy of Sciences
- Fellow of the European Academy of Sciences
- Fellow of the American Association for Advancement of Science
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OUTLINE

1-U2ACN2:
2-NANO-BACKGROUND: FROM BACTERIA TO CELLPHONE

3-NANO-ZnO:SURFACE TENSION TUNABILITY
4-NANO-VO_2: MULTIFUNCTIONALITY

4-NANO-IN NATURE

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MULTISKILLED Human Capital DEVELOPMENT-

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MULTISKILLED Human Capital DEVELOPMENT-

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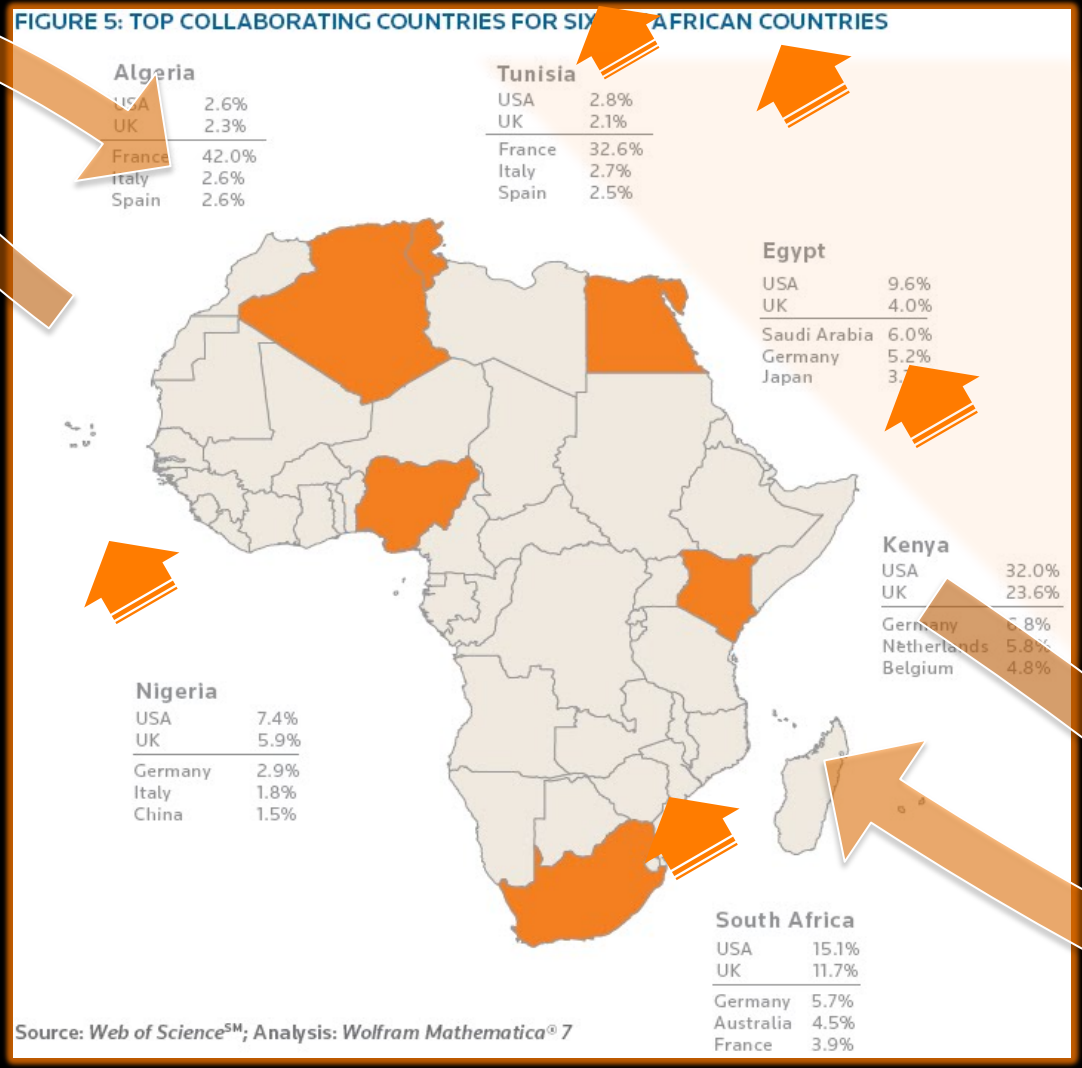

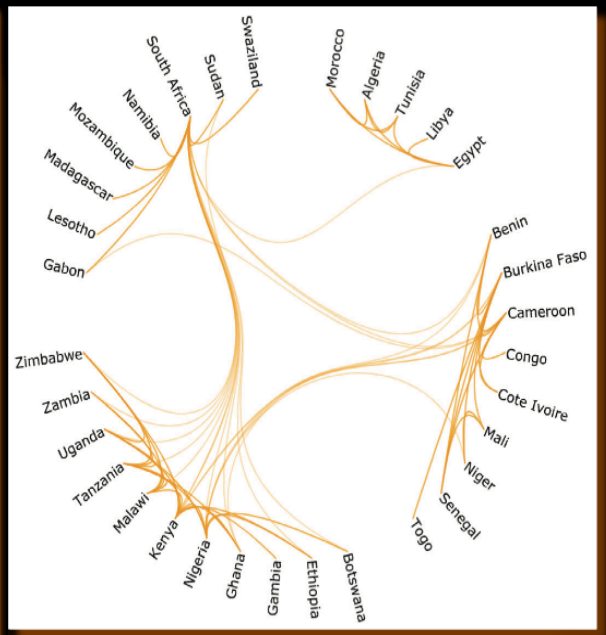

Source: OECD, Nature Publishing, World Economic Forum 2012

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Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Structural and optical properties of nano-structured tungsten-doped ZnO thin films grown by pulsed laser deposition

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U2ACN2: UNESCO UNISA ITLABS/NRF AFRICA CHAIR IN NANOSCIENCES & NANOTECHNOLOGY

RESEARCH FOCUS:

- Nanomaterials for Energy
- Nanophotonics,
- Nanomaterials by green Processing,
- Nanomaterials & biomimics,
- Nanomaterials & Radiations:

I-Nanostructures for neutrons trapping & neutron life time

II-H^+ induced magnetism in Carbon based nanosystems,

III-H^+induced Superconductivity in WO_{3-d} bronzes,

IV-Nano-suspensions by γ-radiolysis,

V-IBA Radiations hardness of nanomaterials.

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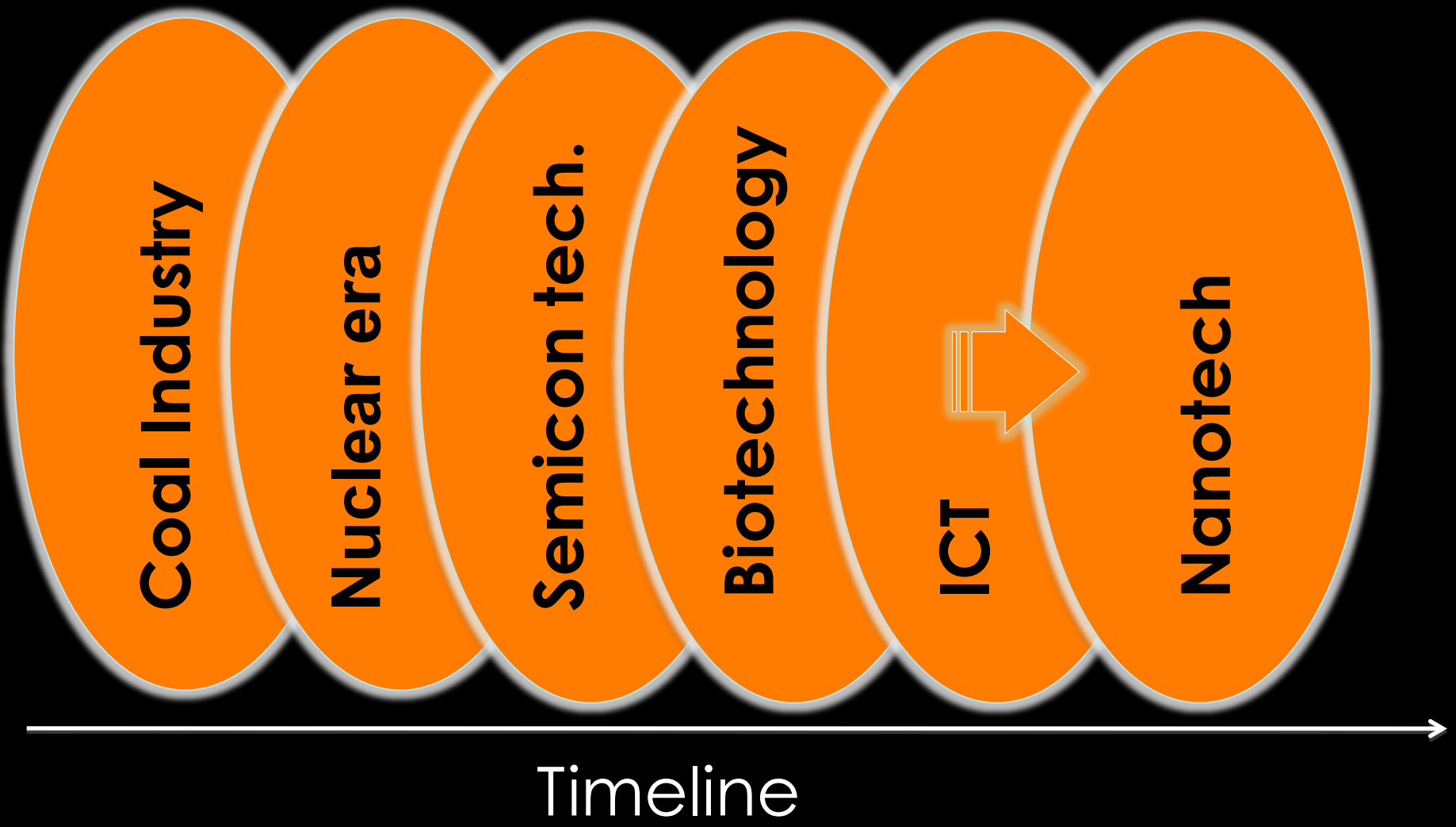
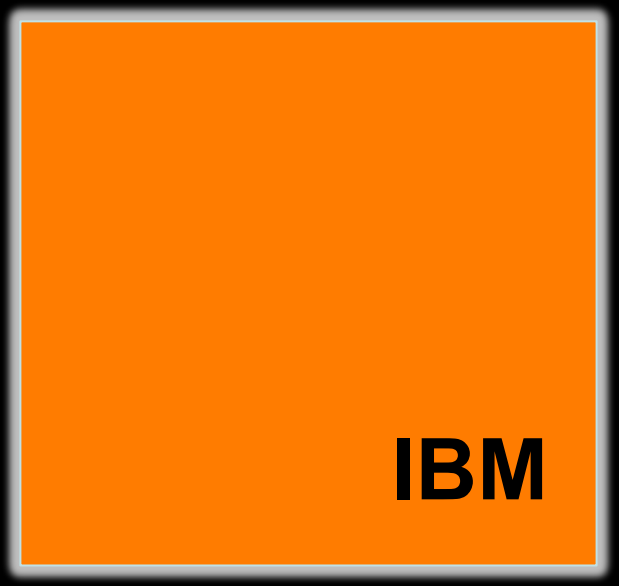
NANO-0:
NANO:BACKGROUND

NANO-BACKGROUND: EVOLUTION



NANO-BACKGROUND: DATA STORAGE



4 589 844 "IBM"= 1 "6M" 1Tb= ? IBM

Data Storage Capacity

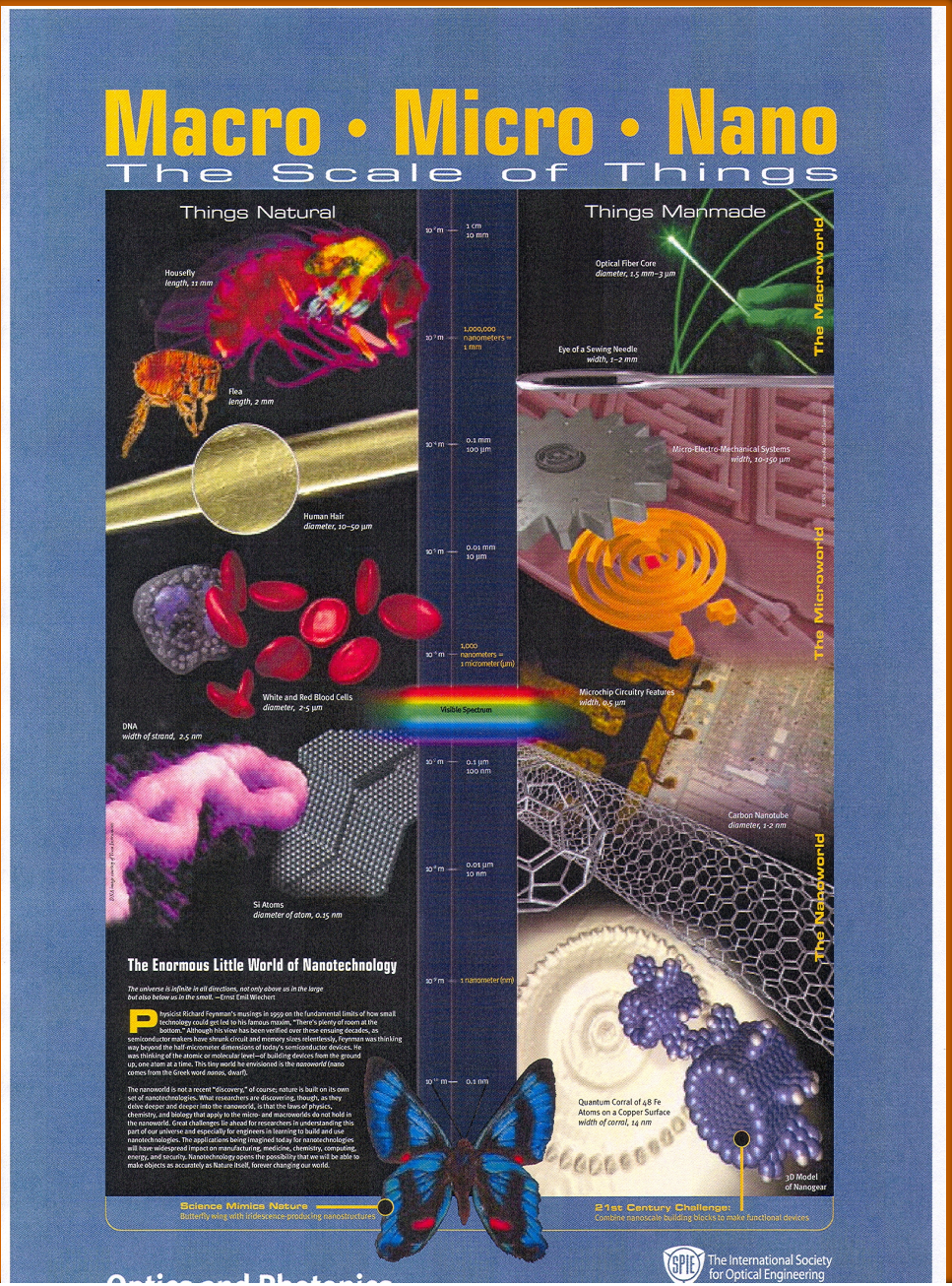
1970 1995 2010

NANO-BACKGROUND: BIO MIMICS LIMITS

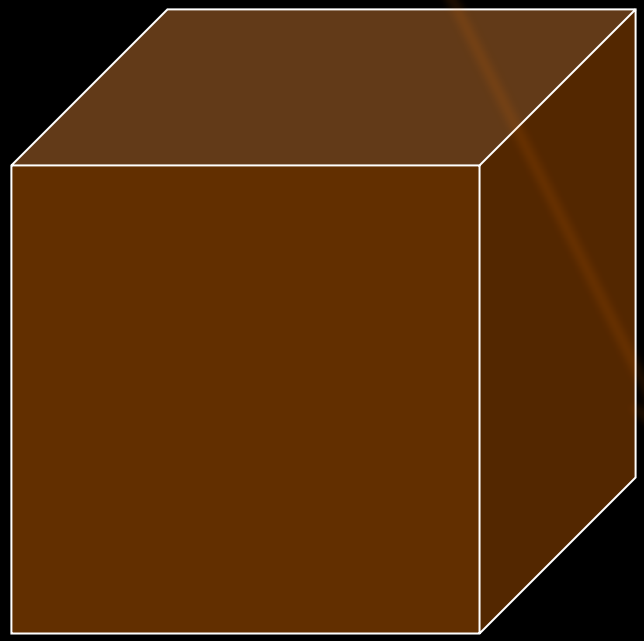
- Human hair
  10-50 μm

- Red blood cell
  2-5μm

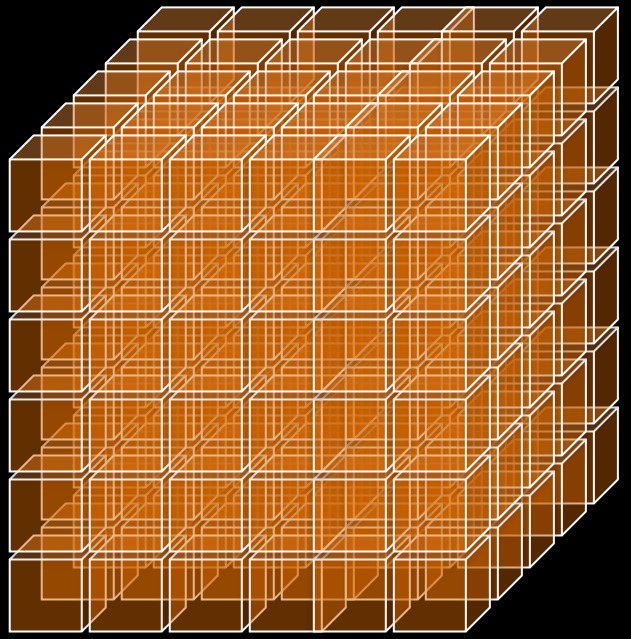
- DNA strand
  2-5 nm



NANO-BACKGROUND: FUNDAMENTALS
SURFACE/VOLUME



L

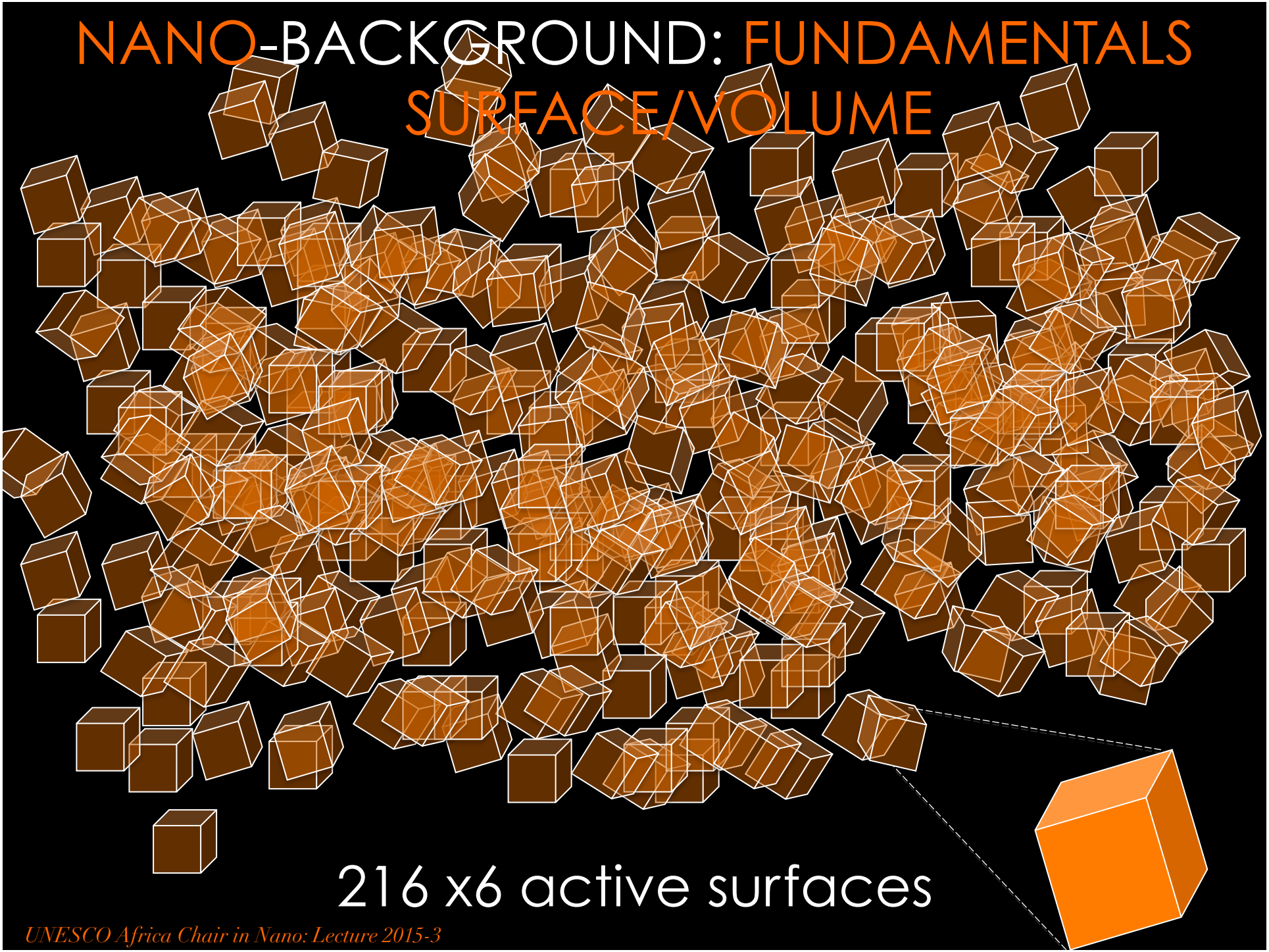


L/6

6x6x6= 216

NANO-BACKGROUND: FUNDAMENTALS

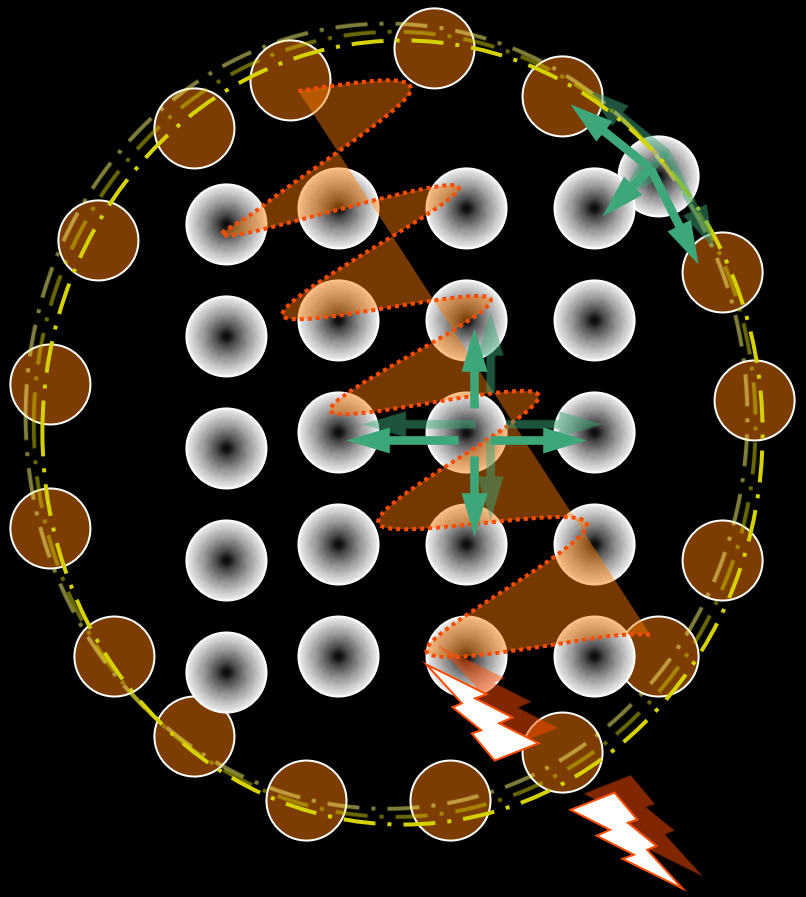
SURFACE/VOLUME



NANO-BACKGROUND: FUNDAMENTALS SURFACE/VOLUME

1 kg of particles of 1 mm^3
has the same surface area as
1 mg of particles of 1 nm^3

NANO-BACKGROUND: FUNDAMENTALS



-3-D Symmetry

Broken for Surface Atoms,

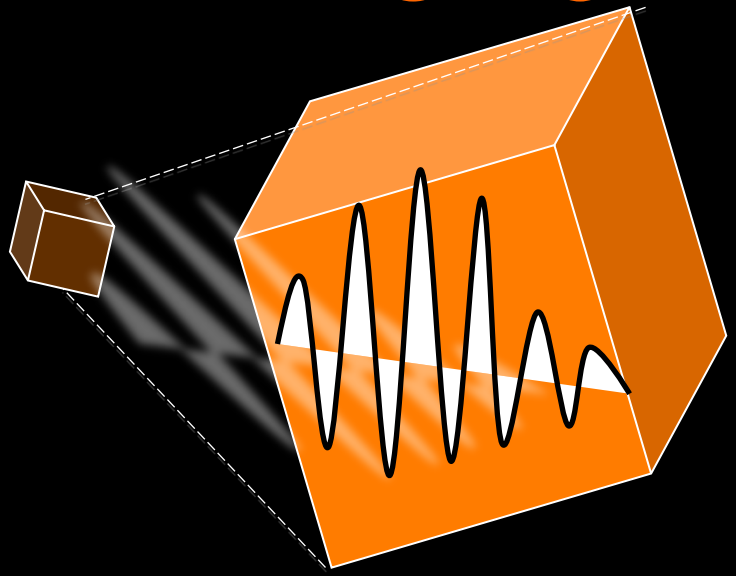
-Localized States

Carriers/ phonons confinement,

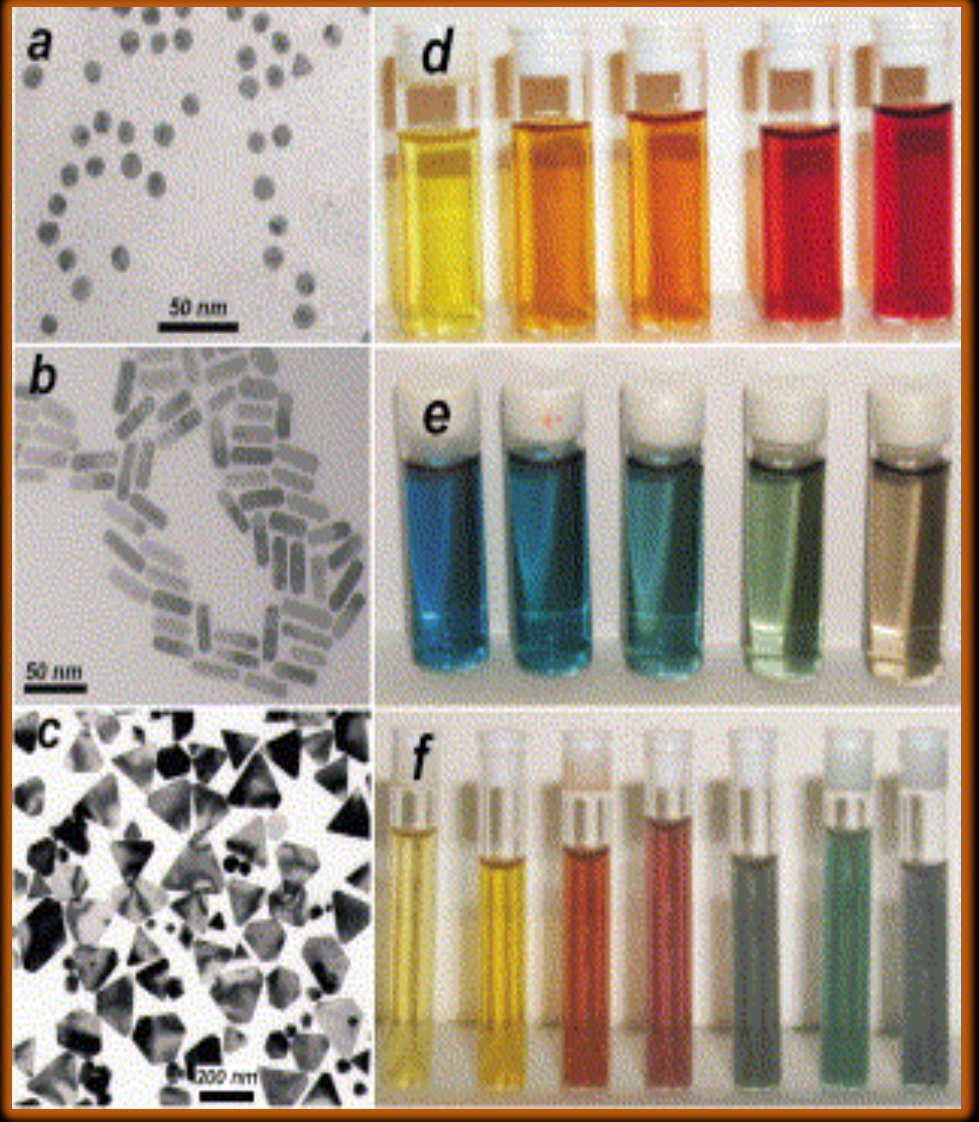
-High Surface/Volume

> 50% "1/ϕ"

NANO-BACKGROUND: FUNDAMENTALS
ELECTRONIC CONFINEMENT

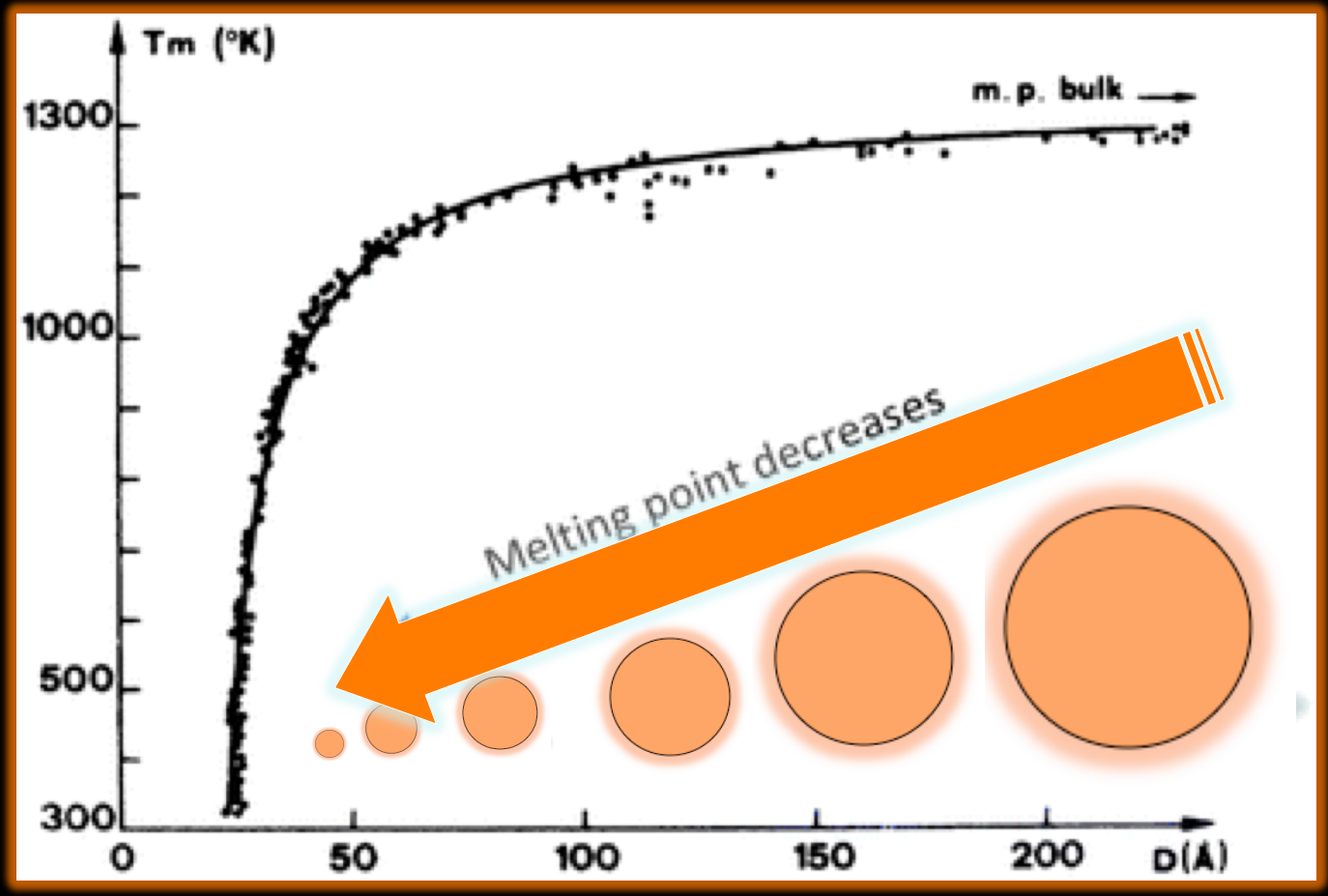


$$\Delta x \cdot \Delta p \cong h/2\pi$$



Liz Marzin, Mater.Today.2004

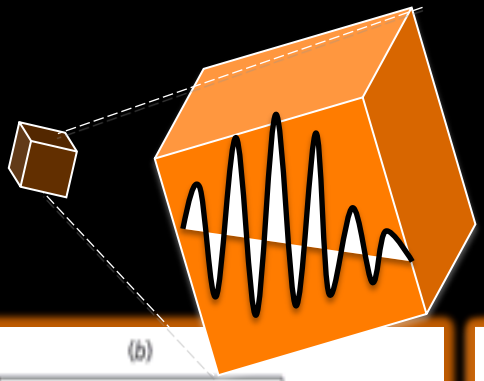
NANO-BACKGROUND: FUNDAMENTALS
SURFACE COORDINATION



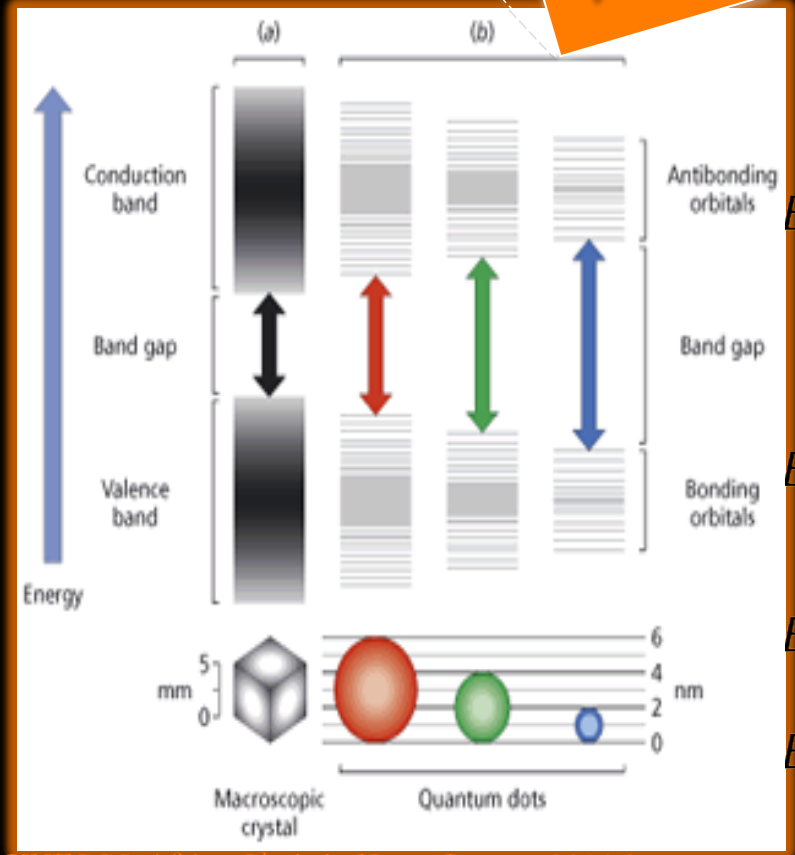
$$T_b/T_m = 1+(2/L\rho_s R)\ [\gamma_s-\gamma_l(\rho_s/\rho_l)^{2/3})]$$

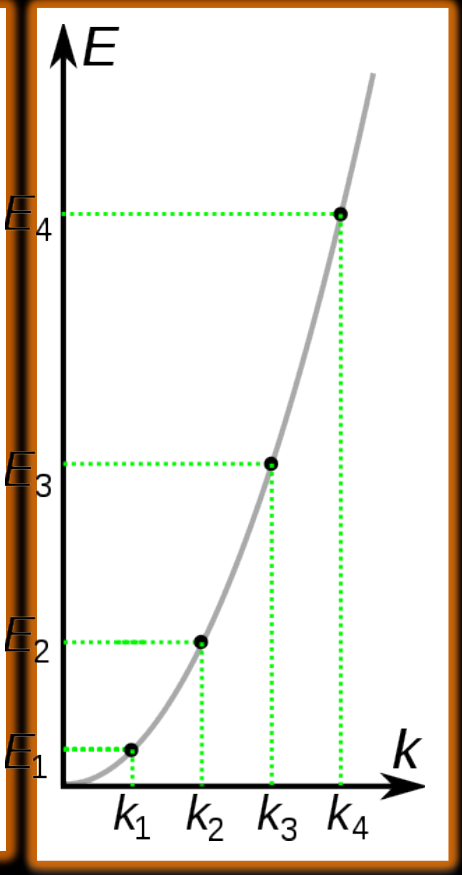
Buffat et al, Phys. Rev.A, 1976

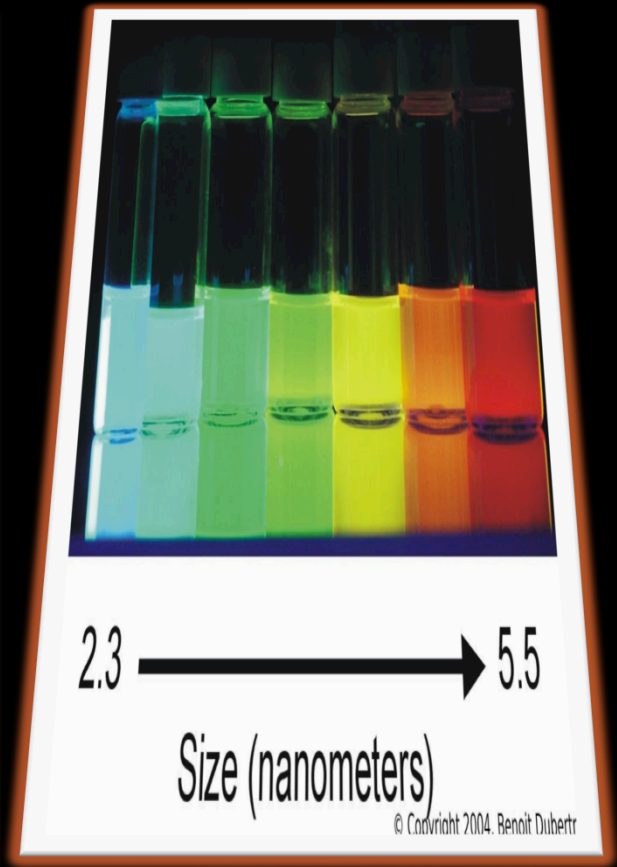
NANO-BACKGROUND: FUNDAMENTALS
ELECTRONIC CONFINEMENT



$$E = n^2k^2/8m\ L^2$$

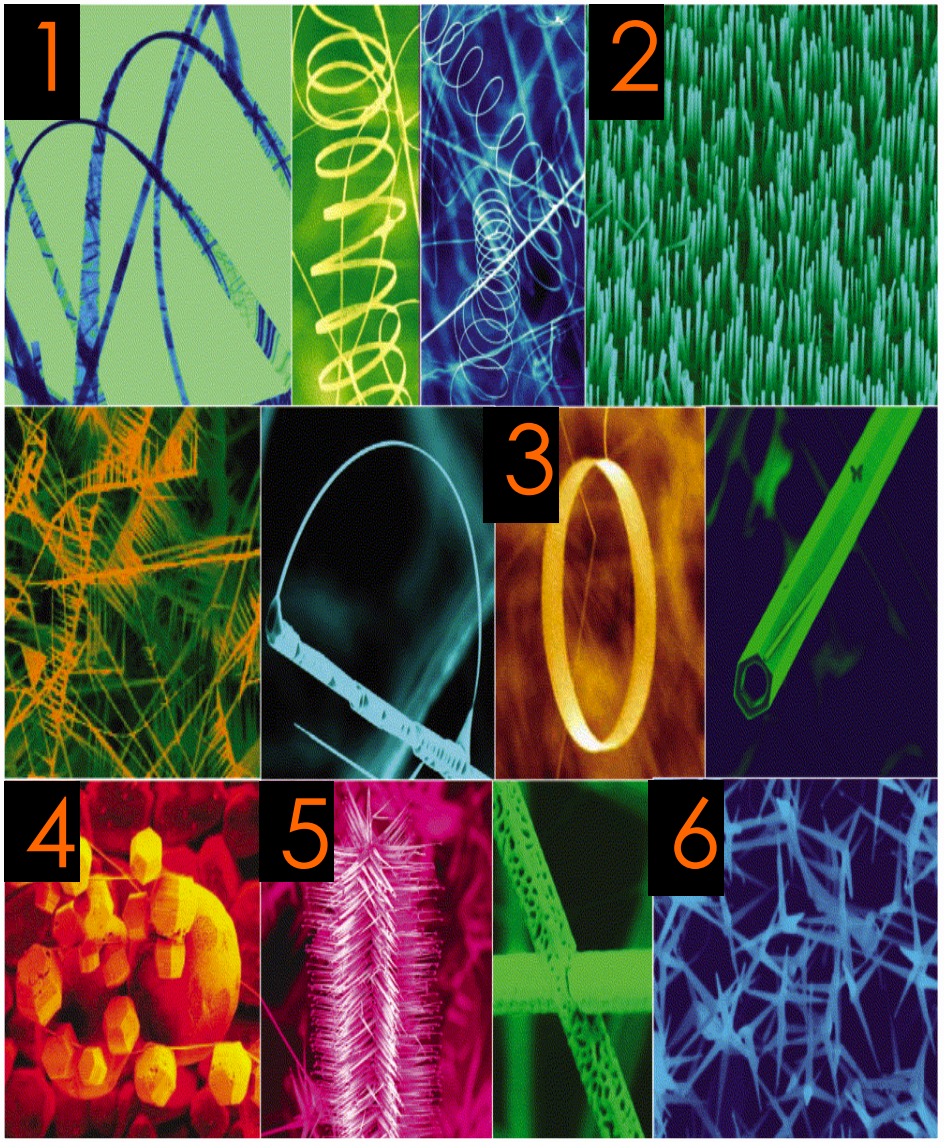






NANO-BACKGROUND: FUNDAMENTALS ELECTRONIC CONFINEMENT

1: Piezoelectrics
2: Field emission
3: Lasing μ-cavity
4: Sunscreen
5: Gas sensing
6: Electro-screening



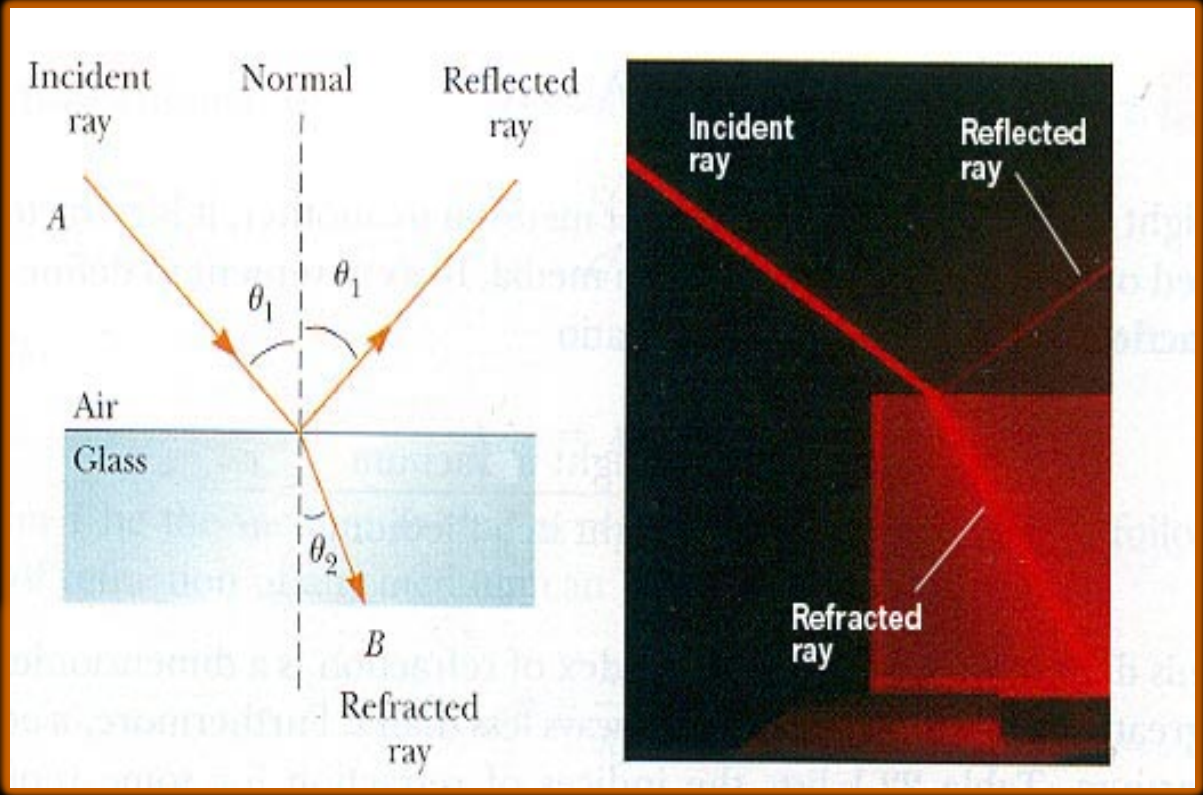
"ZnO", Wang & al, Optics , Mater. Today, 2003

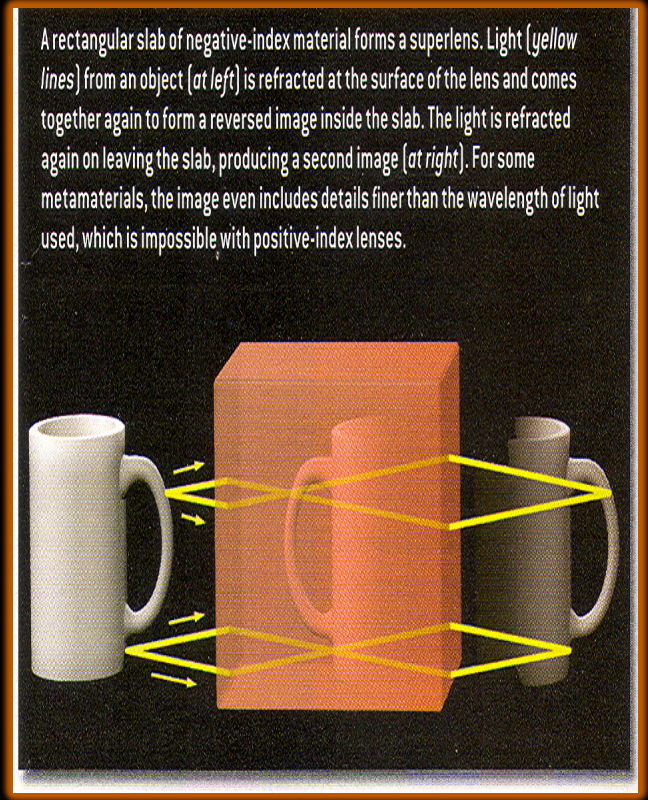
NANO-BACKGROUND: FUNDAMENTALS ELECTRODYNAMICS/ METAMATERIALS

Electric permitivity: ε

Magnetic permeability: μ

$$n = \pm\sqrt{(\varepsilon\ \mu)}$$





NANO-BACKGROUND: FUNDAMENTALS ELECTRODYNAMICS/ METAMATERIALS

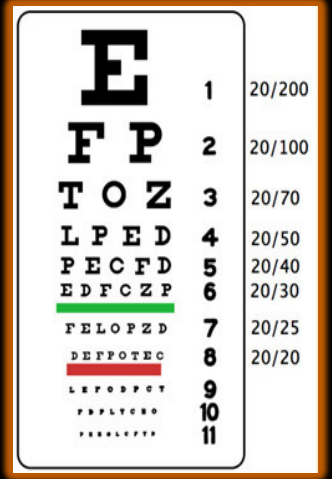
Electric permitivity: $\varepsilon < 0$

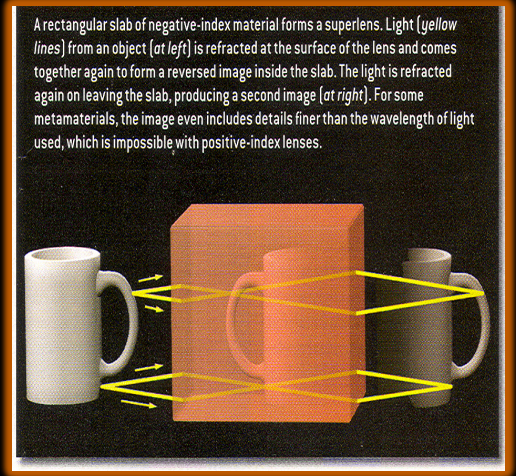
Magnetic permeability: $\mu < 0$

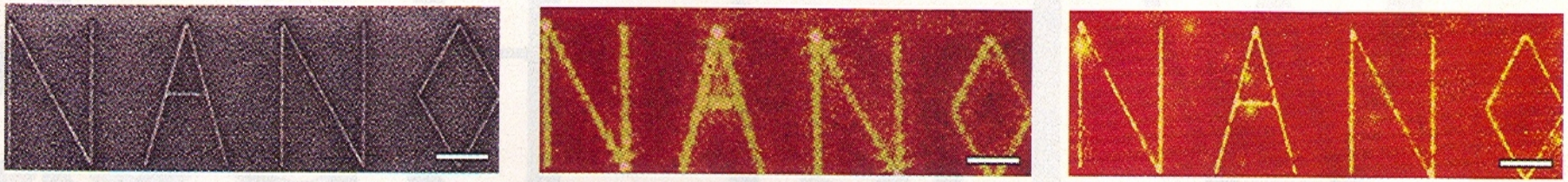
(D. Veselago, 1963, J. Pendry, 2000)

$n = \pm\sqrt{(\varepsilon\ \mu)}$

$n < 0$

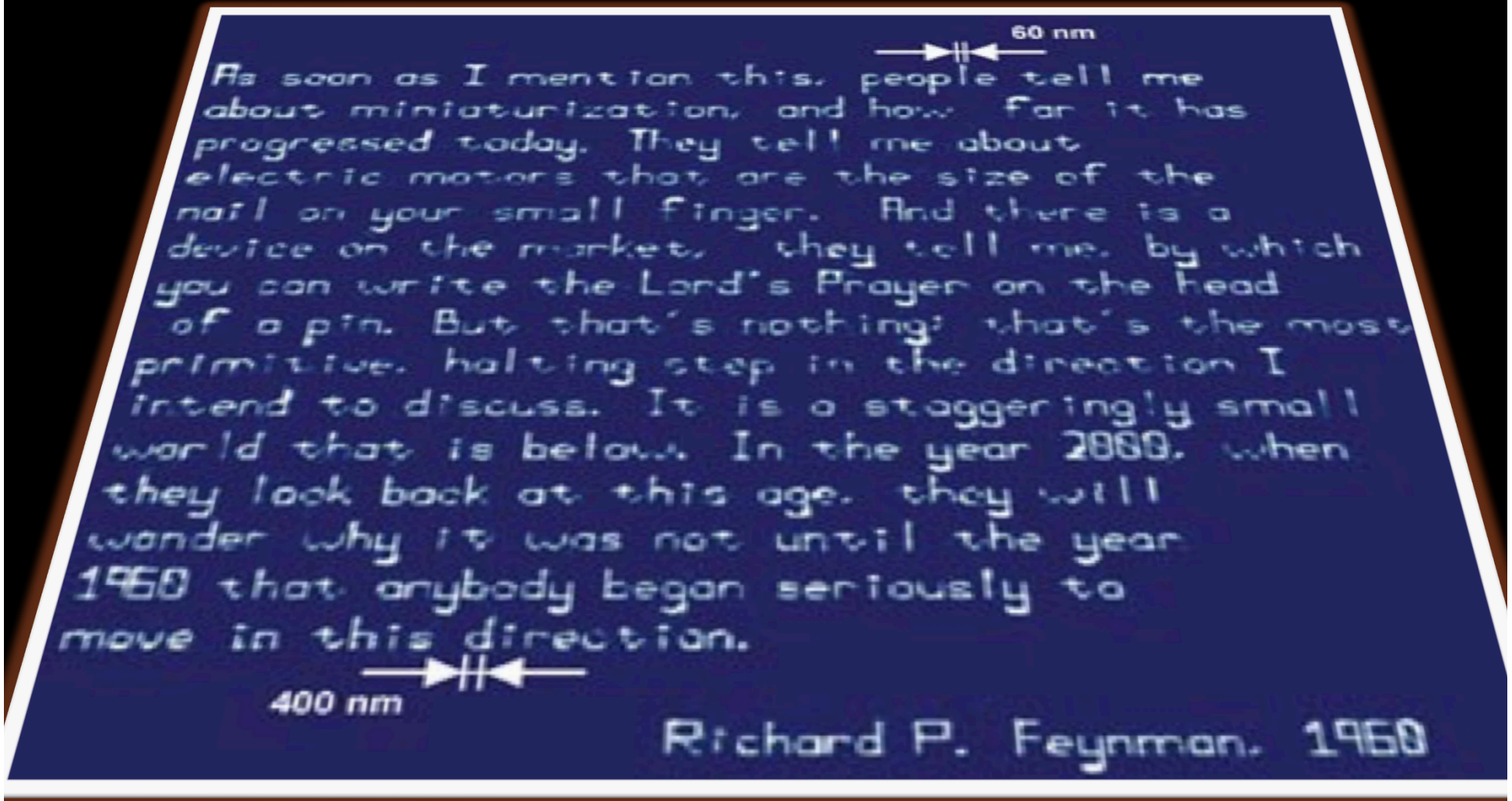






THIN LAYER OF SILVER acts like a superlens over very short distances. Here the word "NANO" is imaged with a focused ion beam (*left*), optically without a superlens (*middle*) and optically with a 35-nanometer layer of silver in place (*right*). Scale bar is 2,000 nanometers long. With the superlens, the resolution is finer than the 365-nanometer wavelength of the light used.

NANO-BACKGROUND: FUNDAMENTALS
TOOLS: ATOMIC MANIPULATION



NANO-BACKGROUND: FUNDAMENTALS ADVANCED SYNTHESIS/CHARACT. TECHS.

Variety of cost effective/mass scale syntheis techs.
Fore front characterization techs.

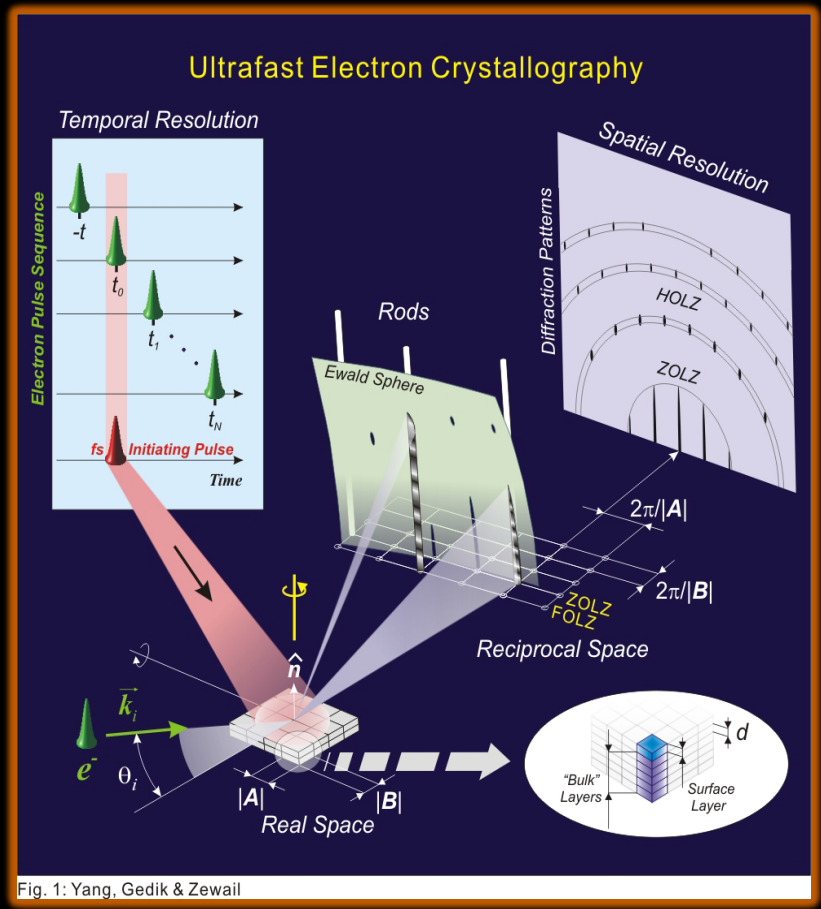
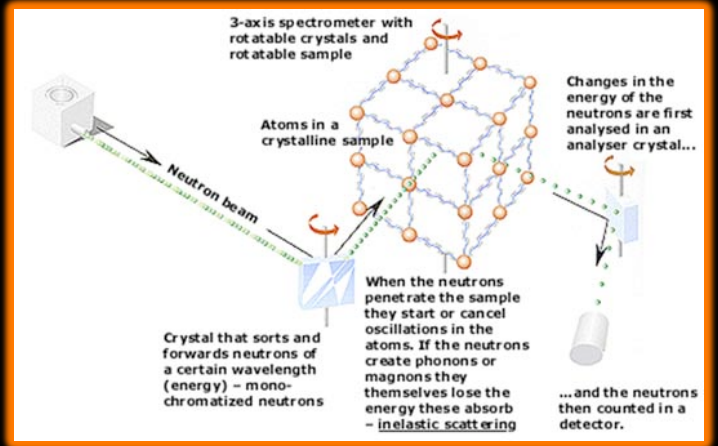
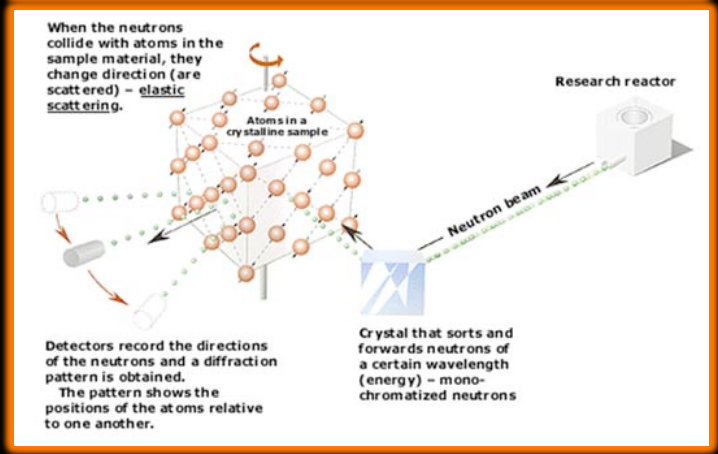


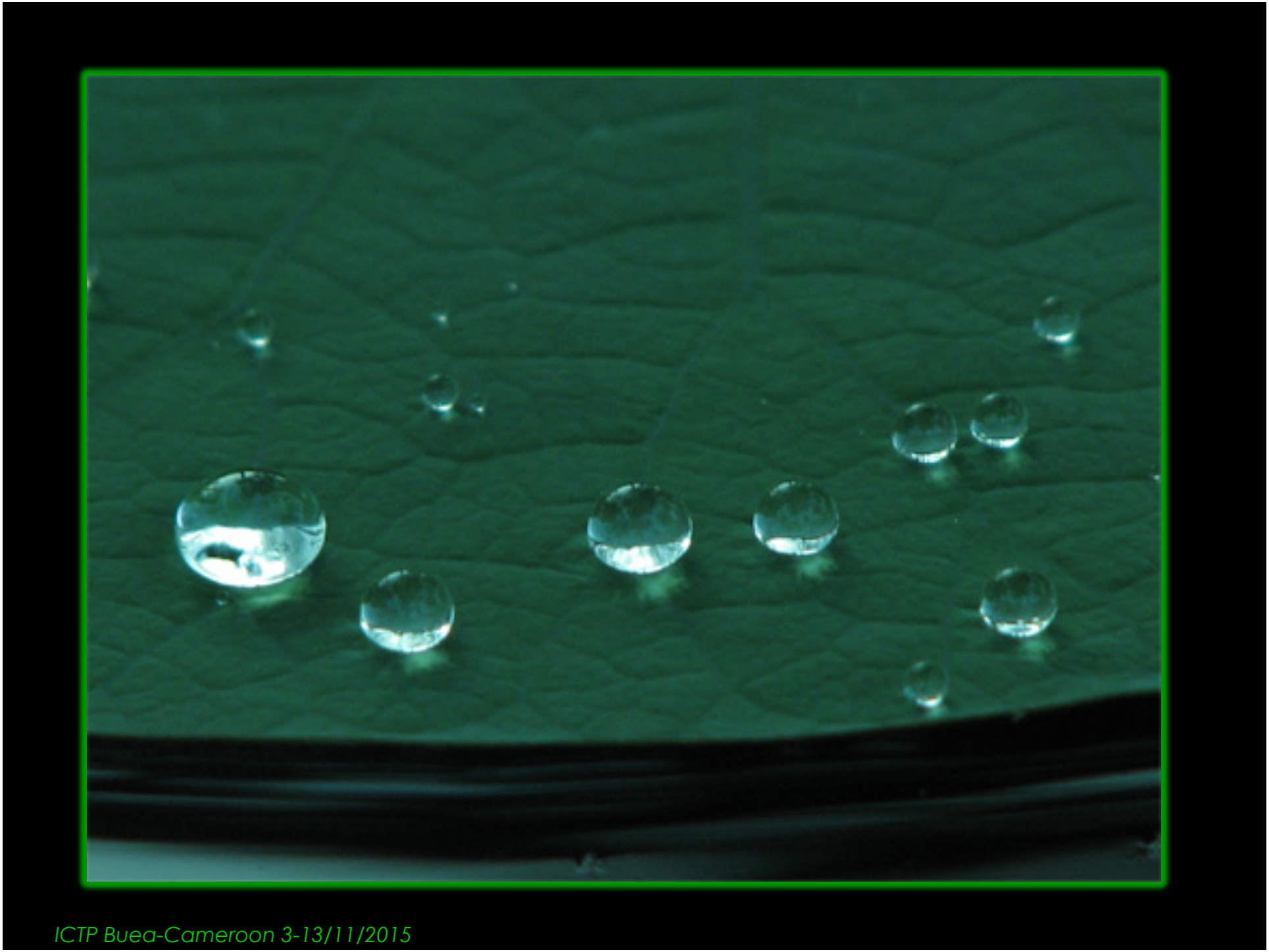
Fig. 1: Yang, Gedik & Zewail



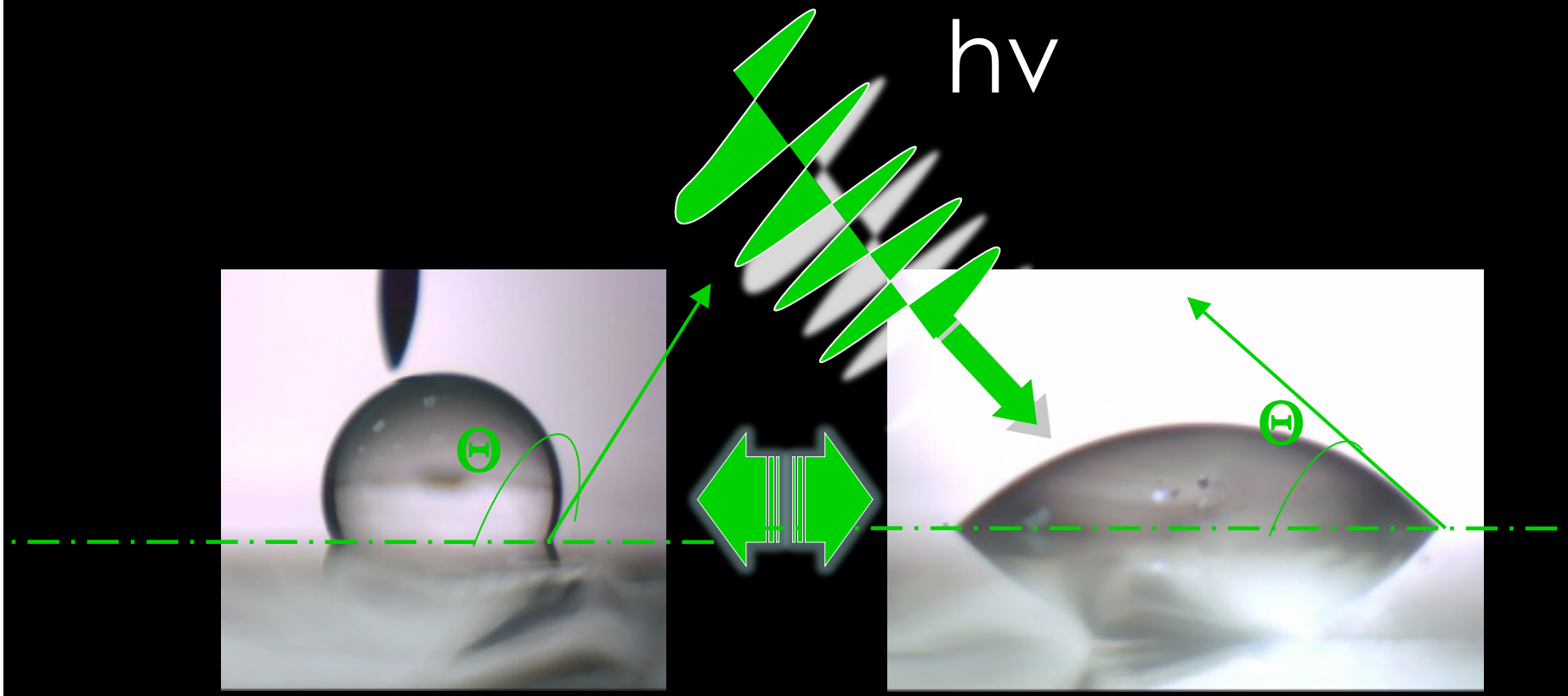


Yang, Gedik & Zewail

NANO-1:
TUNABLE SURFACE TENSION

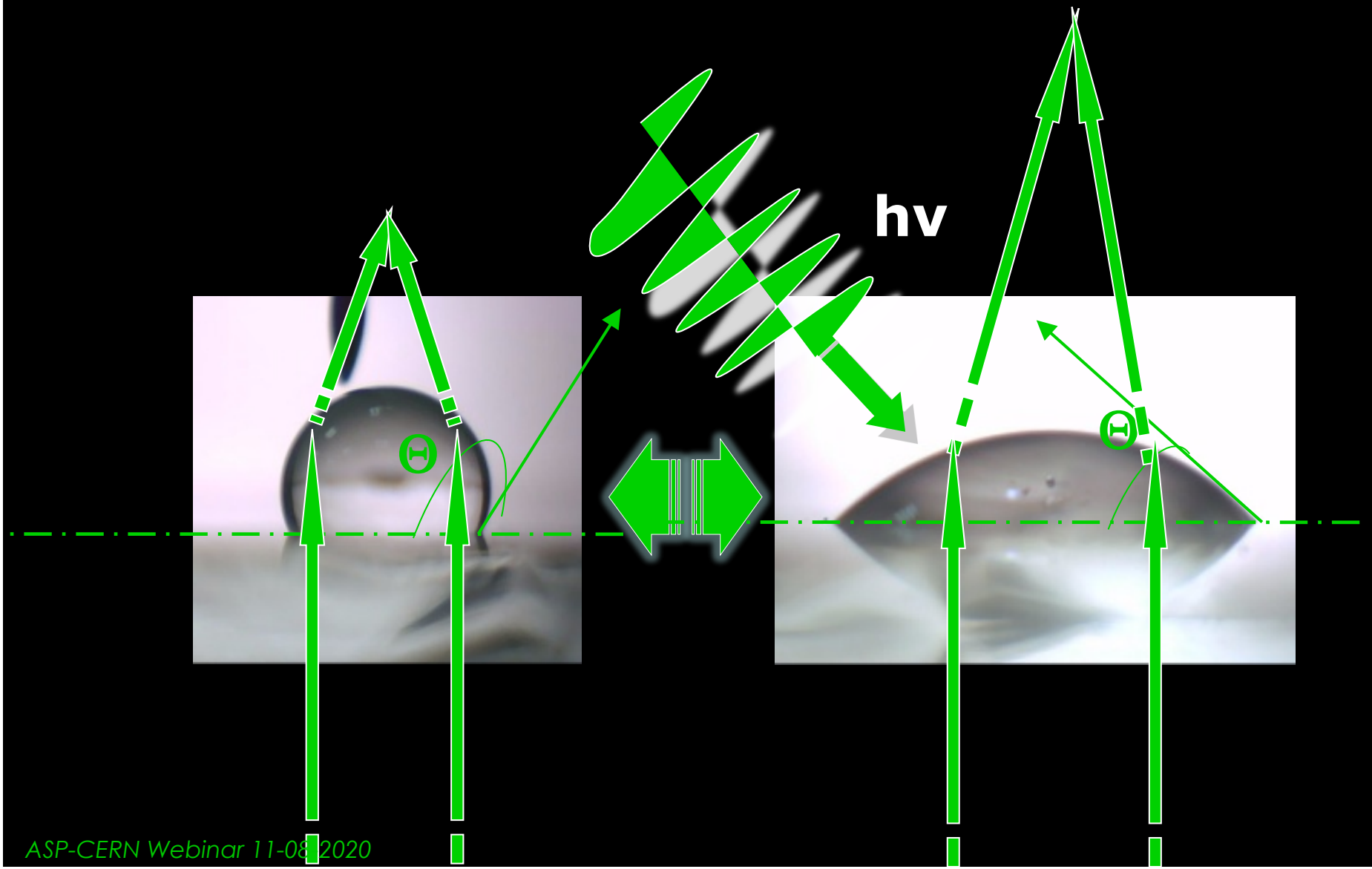


NANO: LOCALIZATION & CONFINEMENT
–Surface Tension Tunability



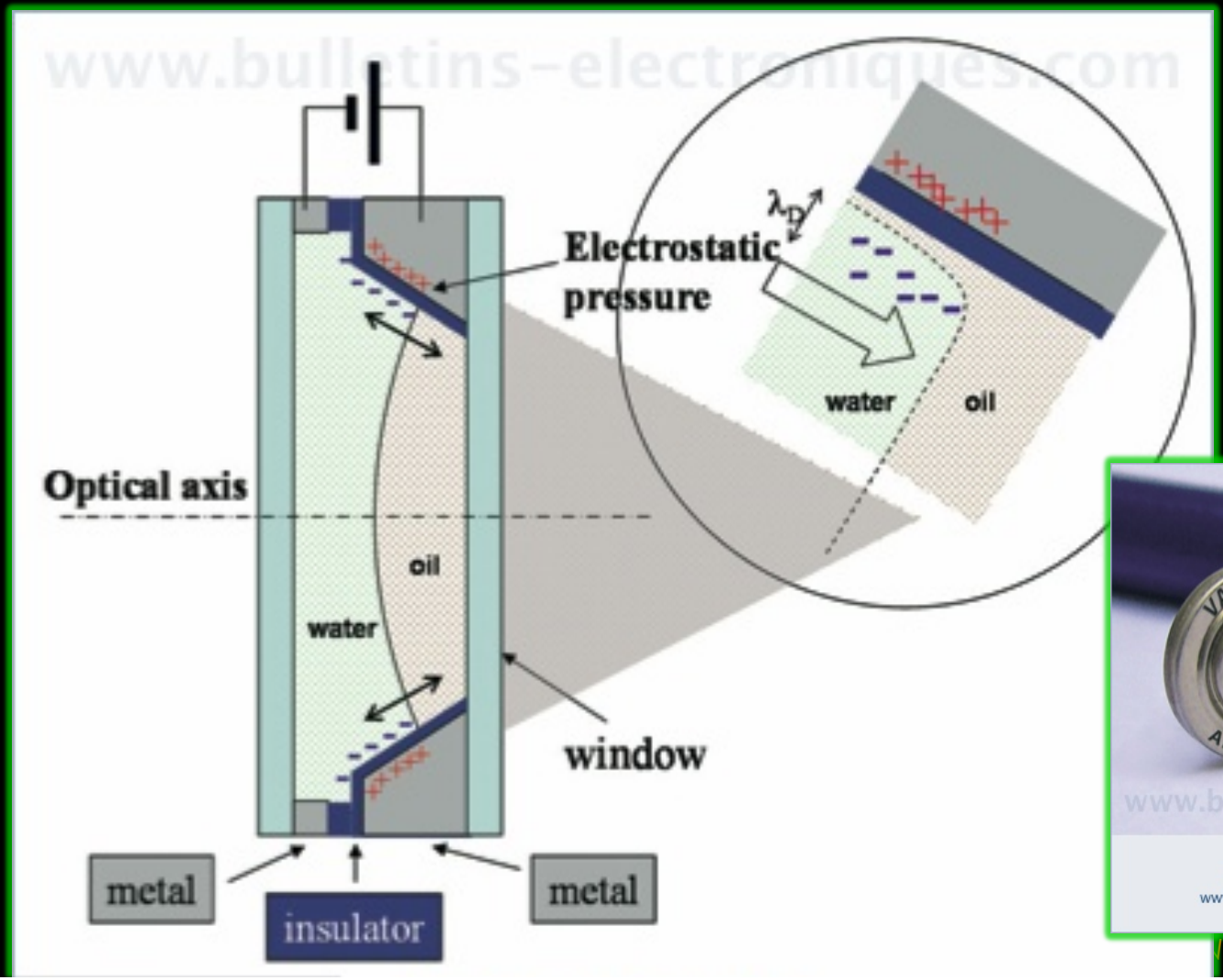
NANO: LOCALIZATION & CONFINEMENT

- Liquid lens with tunable focus "f"

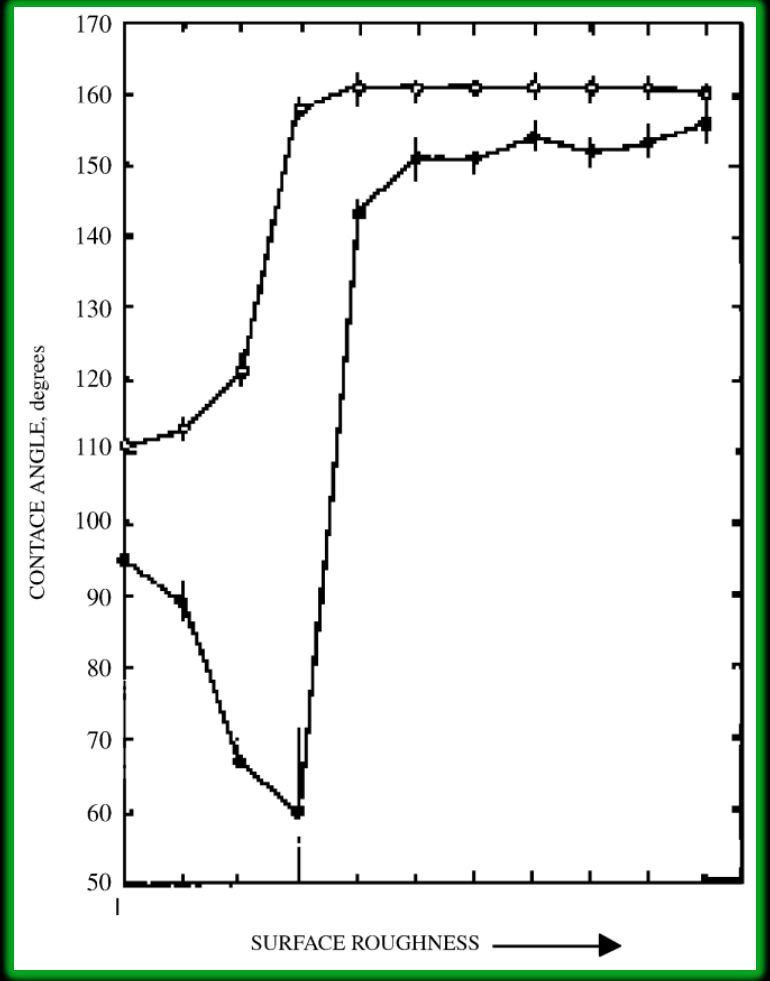


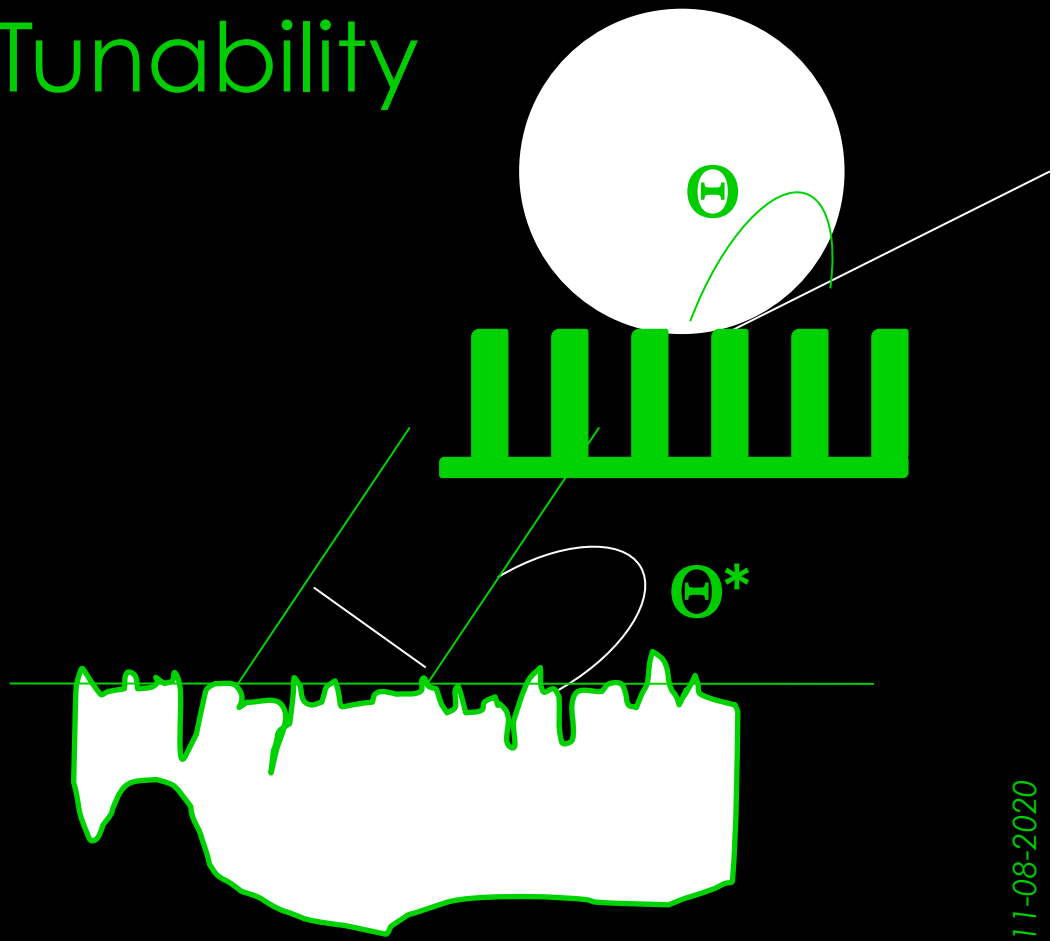
NANO: LOCALIZATION & CONFINEMENT

- Liquid lens with tunable focus "f"
- "Varioptic/ Singapore" liquid lens



NANO: LOCALIZATION & CONFINEMENT –Surface Tension Tunability





$$\cos\Theta^* = f_1 \cos\Theta_1 + f_1 \cos\Theta_2)$$

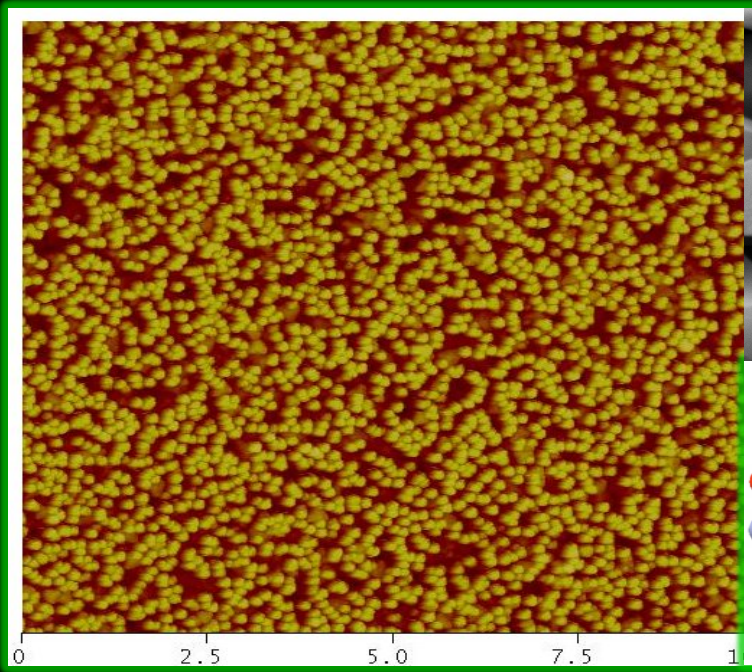
Wenzel/Cassie model

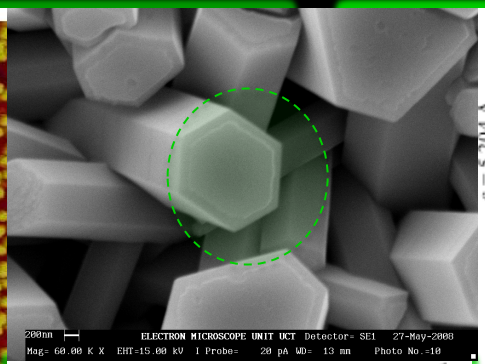
-Wenzel, R.N. Industrial and Engeneering Chemistry, 1936, 28, 988-994.
-Cassie, A.B.D.; Baxter, S. Transactions of the Faraday Society, 1944, 40, 546-551
- Johnson R.E., Dettre R.H., Adv. Chem. Ser.43, 1964, 112-135 [H_2O/ Wax substrates]

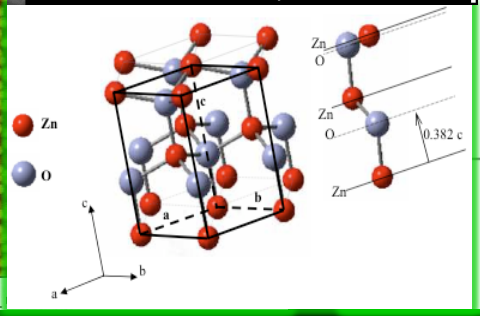
NANO: LOCALIZATION & CONFINEMENT –Surface Tension Tunability

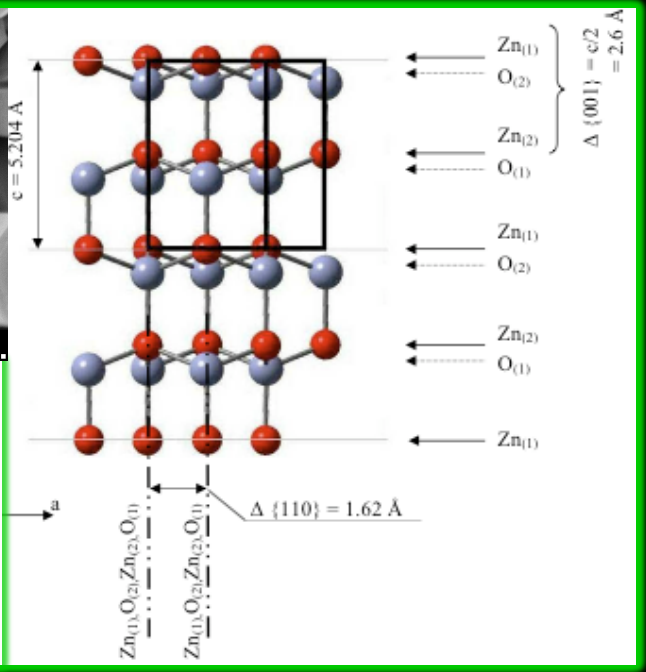
- ZnO: Wurtzite structure
- O-lattice shifted by 0.382 fraction of cell unit heigth "c" from te Zn-latt.
- Reference: Basal Hexagonal plane (001)

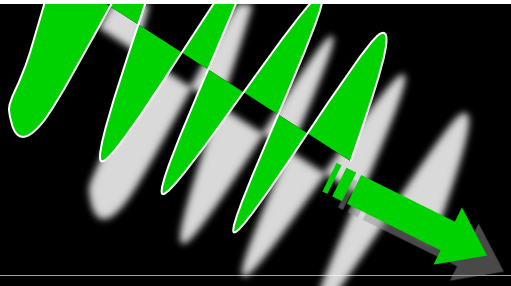
Zn sites: (000) and (2/3, 1/3,1/2)
O sites: (0,0,0.382) and (2/3, 1/3,1/2+0.382)



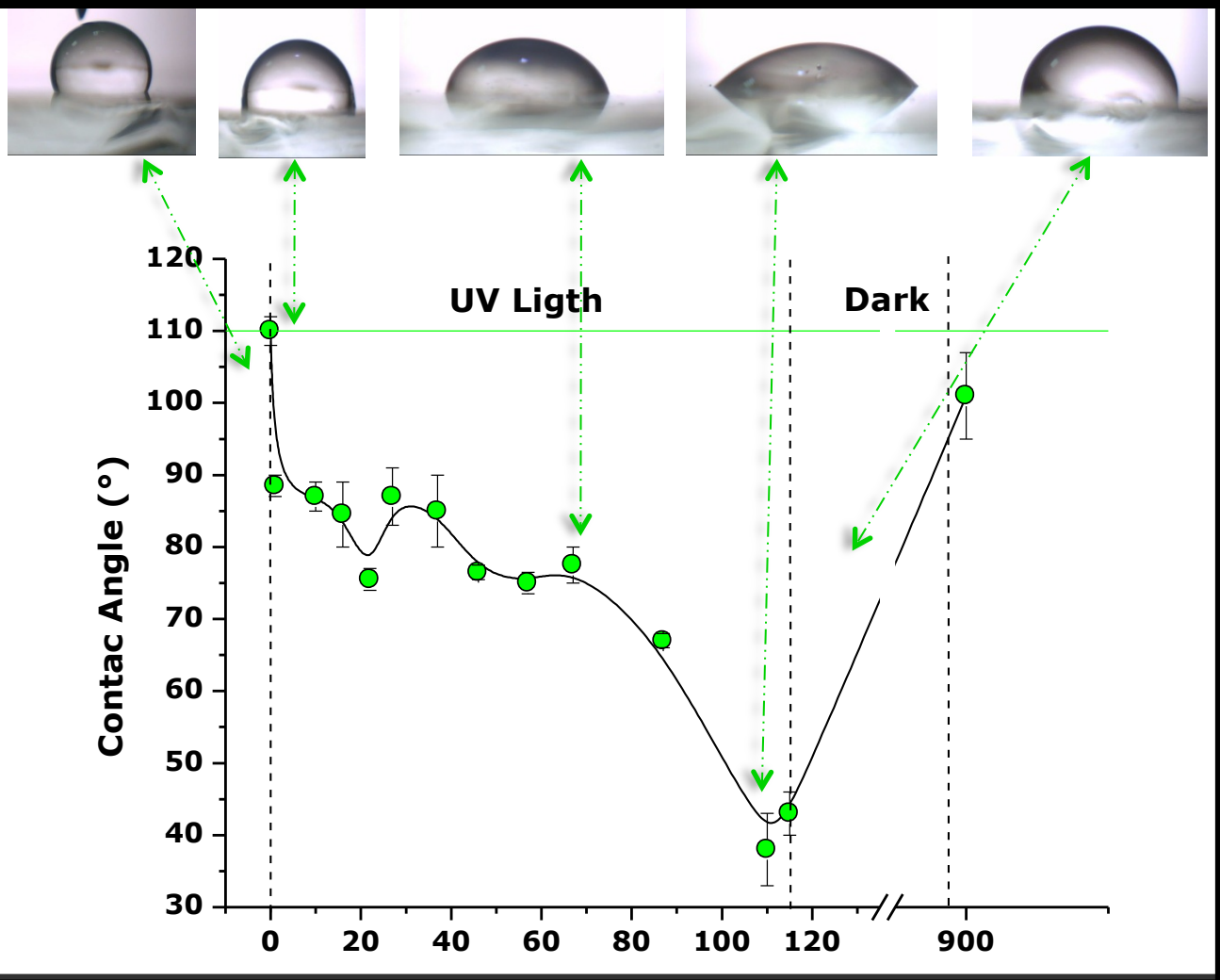






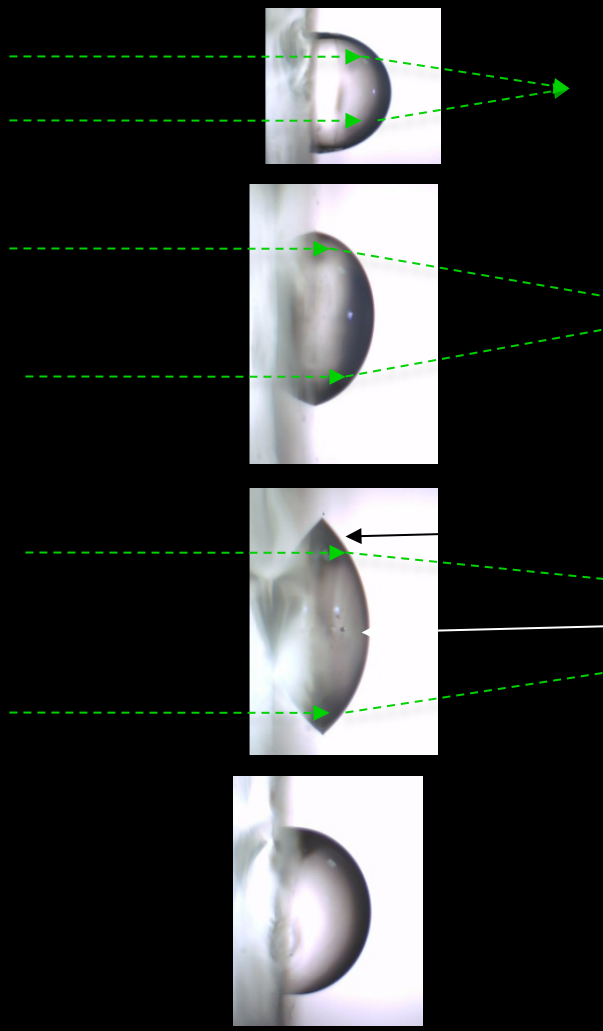


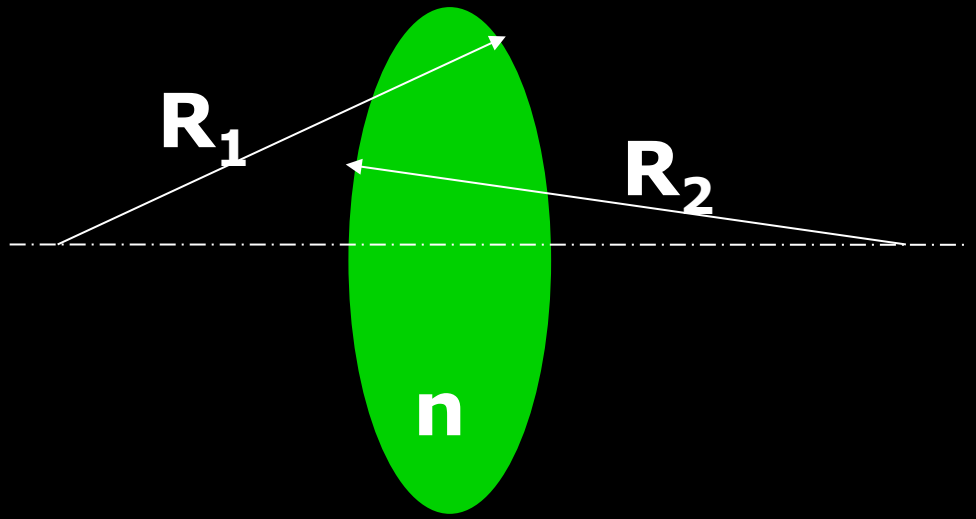
No UV 1 min UV 63 min UV 115 min UV No UV: Dark



NANO: LOCALIZATION & CONFINEMENT

- Liquid lens with tunable focus "f"

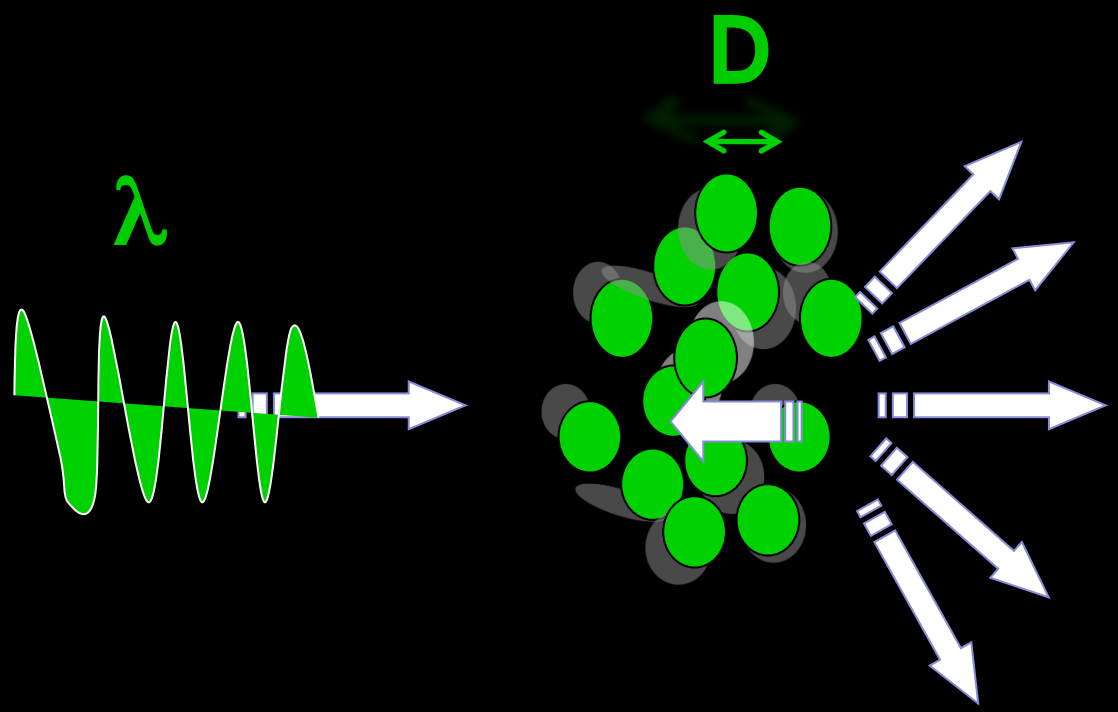




f

$$1/f = (n-1)(1/R_1 - 1/R_2)$$

NANO: LOCALIZATION & CONFINEMENT –Surface Tension Tunability



≠ Scattering cases

•Rayleigh type

$s \propto 1/\lambda^4$, $D < \lambda$

•Mie type $D \cong \lambda$, not analytically solvable for arbitrarily shapes

•Anderson loc.:
½ disordered syst.
Random walk type

NANO-2: MOTT-TRANSITION & MULTI-FUNCTIONALITY

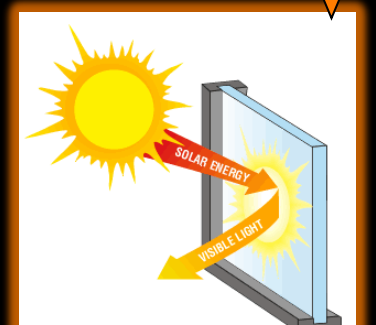
NANO: MOTT PHASE TRANSION

NANO: MOTT PHASE TRANSION

nano-scaled oxides

O_2 CONSUMPTION

ELECTRIC RESISTANCE



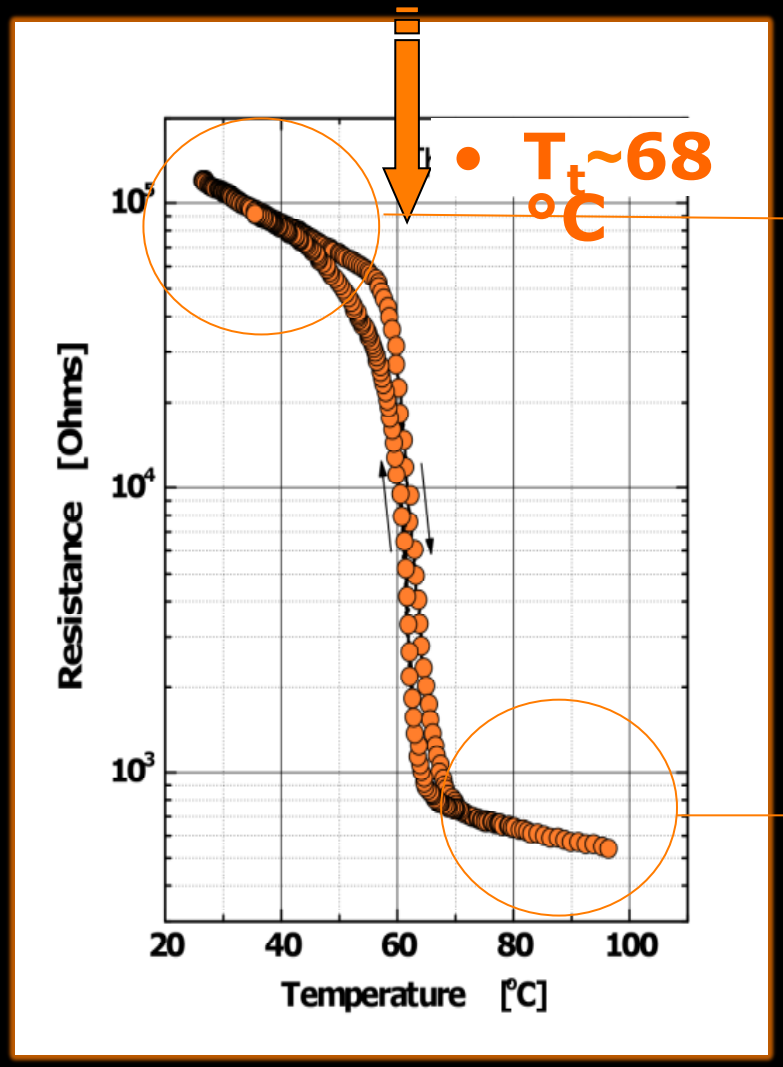
Heating

Cooling

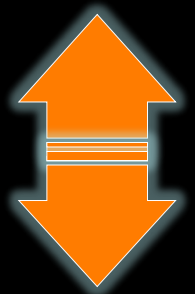
TEMPERATURE

NANO: MOTT PHASE TRANSION

- VO_2 & bandgap tunability



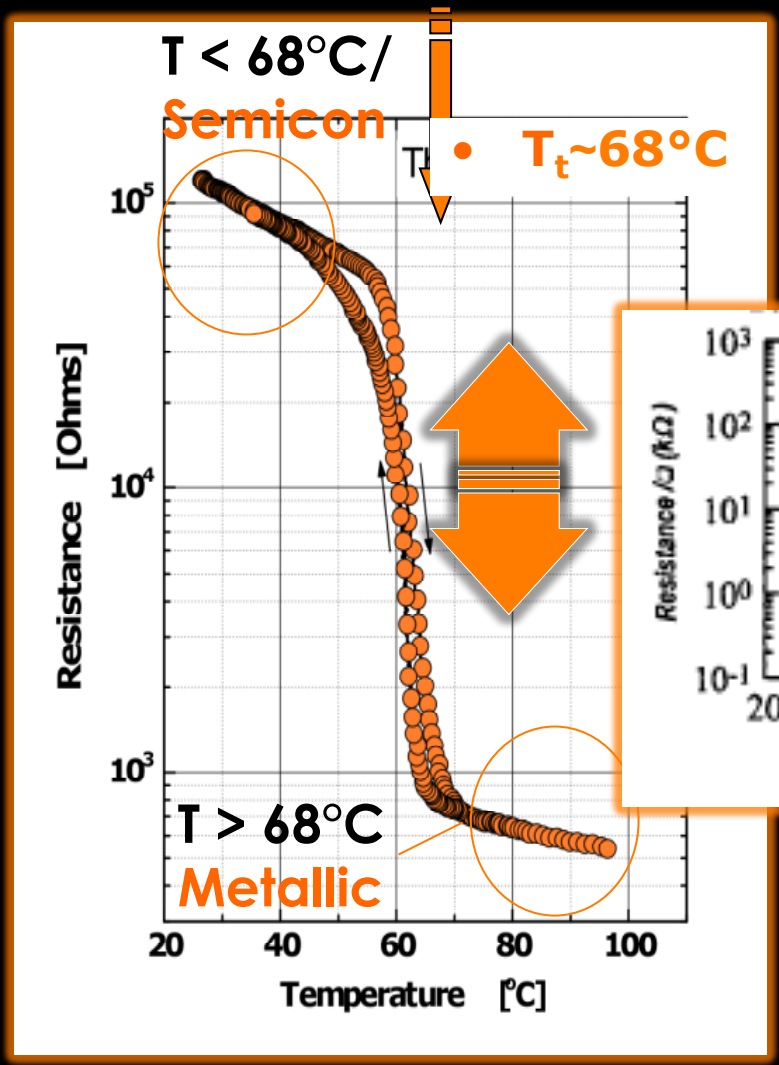
T < 68°C/
Semiconductor

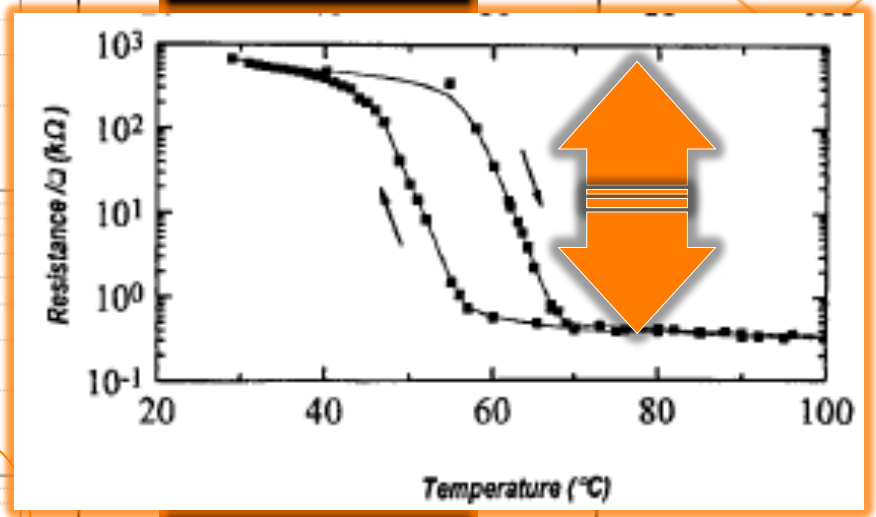


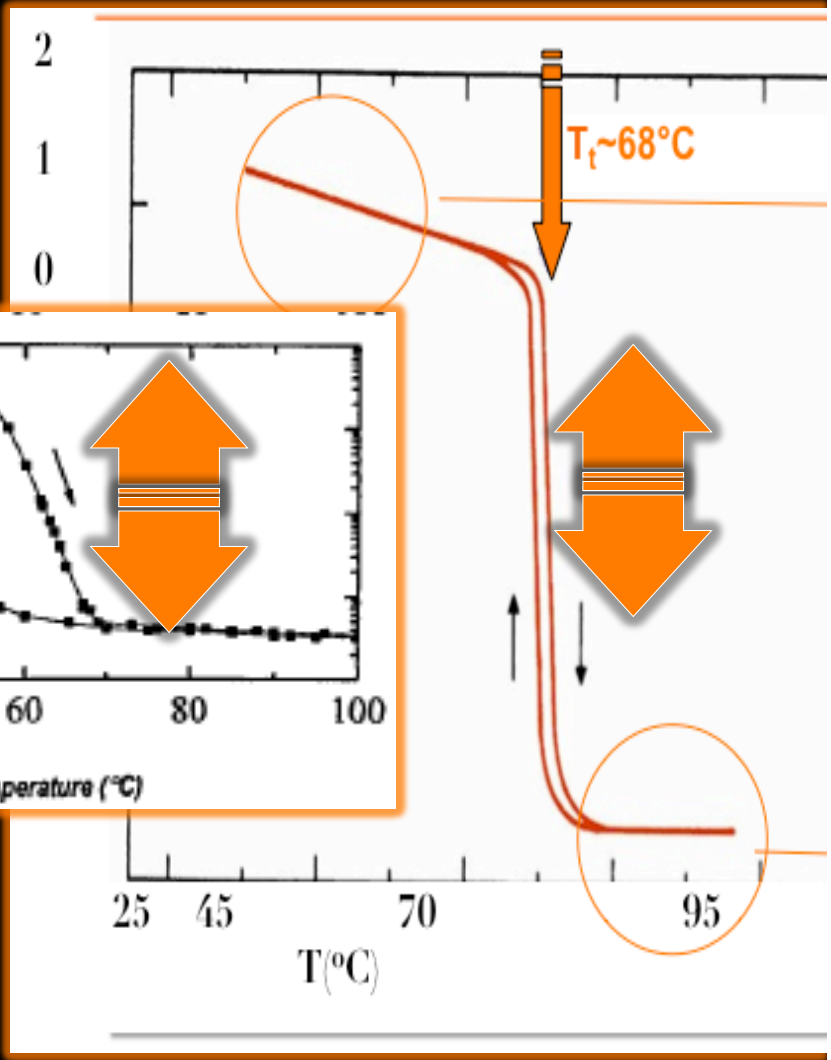
T > 68°C
Metallic

NANO: MOTT PHASE TRANSION

- VO_2 & bandgap tunability
- Quality of the 1st order Mott eletronic transition







NANO: MOTT PHASE TRANSION

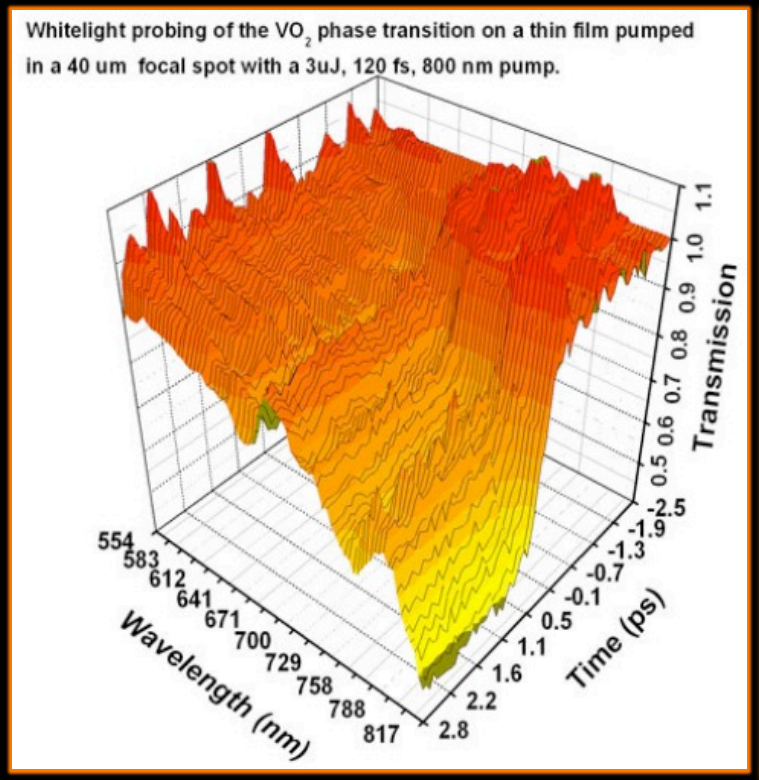
–Mott nano-scaled oxides

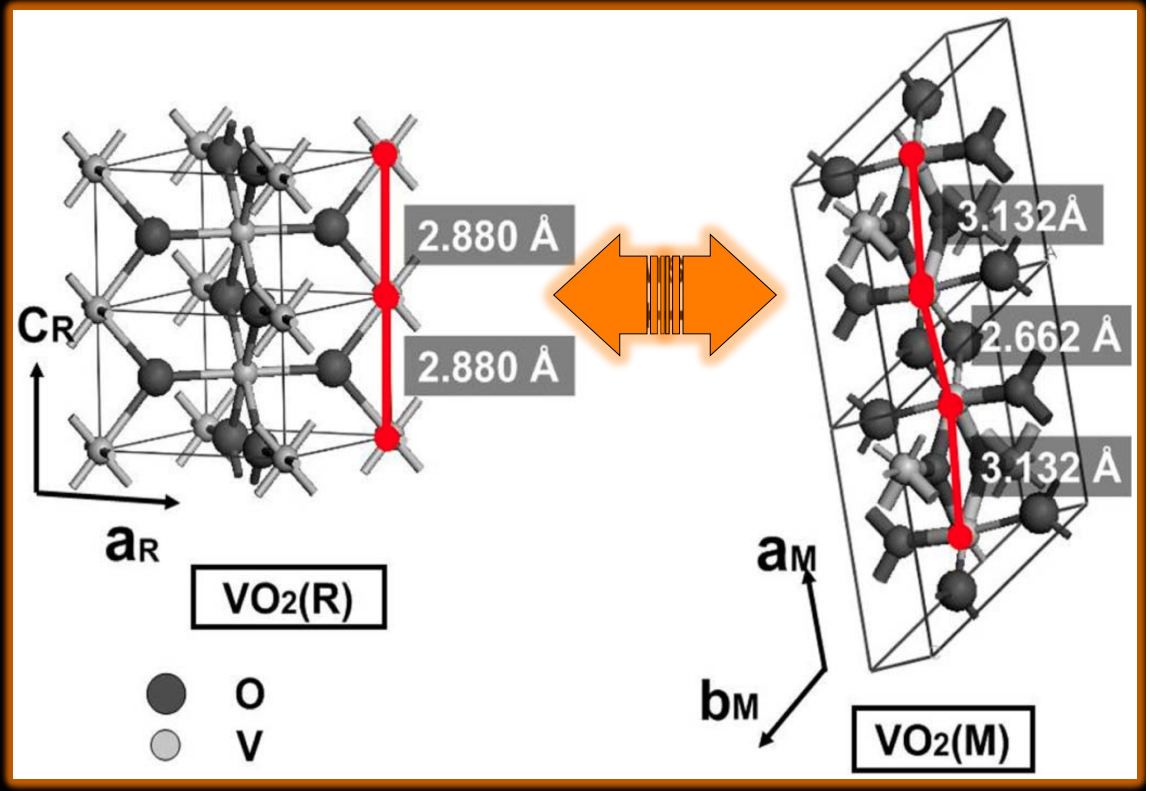
1959: F. J. Morin, Phys. Rev. Lett. **3,** 34,
1968: Sir N. Mott, various seminal contributions.
1968: D. Adler, Rev. Mod. Phys. 40 (4) 714.
1975: 15A. Zylbersztejn and N. F. Mott, Phys. Rev. B **11,** 4383.
1994: Sella & Maaza, Maters. Coatings Tech., 23, 1750.
2000: M. Maaza et al, Optical Materials 15, 41-45 .
2005: S. Biermann et al, Phys. Rev. Lett. **94,** 026404.
2004: A. Cavalleri, & al, PRB 70,161102. "Phase transition measurements: 150 fs"
2005: D. Baum & A. Zewail. "Time resolved/4-D crystallography"
2007: M. M. Qazilbash et al, Science **318,** 1750.
2007: D. Ruzmetov et al, Phys. Rev. B **75,** 195102.
2007: K. Nagashima, T. Yanagida et al, J. Appl. Phys. **101,** 026103.
2008: A. Sharoni, J. G. Ramirez, and I. K. Schuller, Phys. Rev. Lett. **101,** 026404.
2008: G. Willinger et al, Nano Lett. **8,** 4201.
2009: E. U. Donev, R. Lopez, L. C. Feldman, J. R. F. Haglund, Nano Lett. **9,** 702,
2010: A. C. Jones et al, Nano Lett. **10,** 1574.
2011: A. Tselev, et al, Nano Lett. **10,** 2003.
2012: M. Maaza, T. Kerdja et al, Optics Comms, Vol. 285, Issue 6, 1190-1193.
2014: S. Biermann et al, Phys. Rev. Lett. **94,** 026404.

NANO: MOTT PHASE TRANSION

VO_2: Mott type oxide/ Reversible MIT @ T=67.8°C

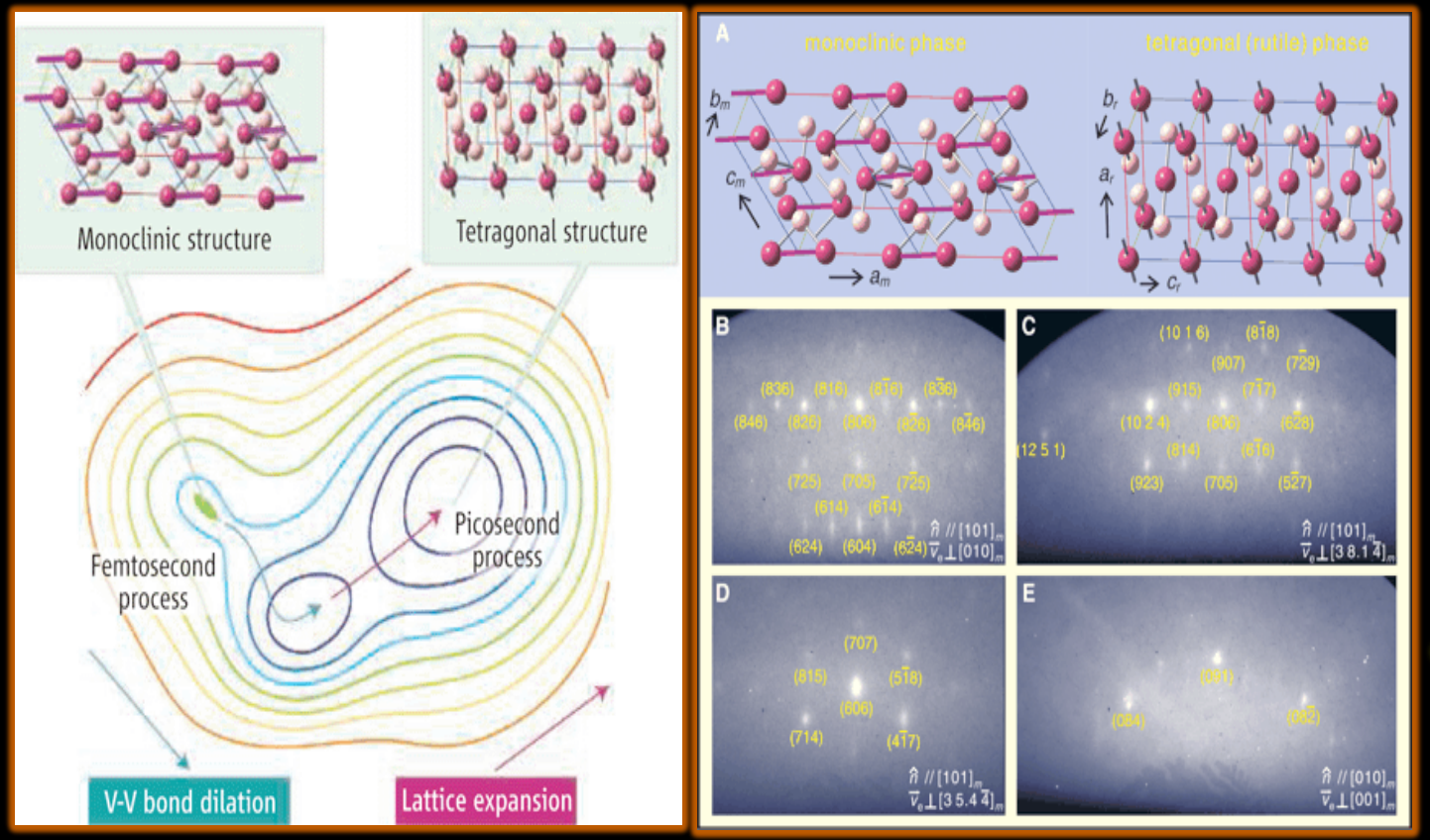
VO_2:Utrafast Reversible MIT transition τ_{VO2}=120 fs





- VO_2(M): insulator, IR transparent, monoclinic phase
- VO_2(R): metallic, IR reflective, rutile phase
- ΔR electrical resistivity is 10^5 below/above τ_{VO2}

NANO: MOTT PHASE TRANSION
–Mott nano-scaled oxides



Localized electrons

V4+

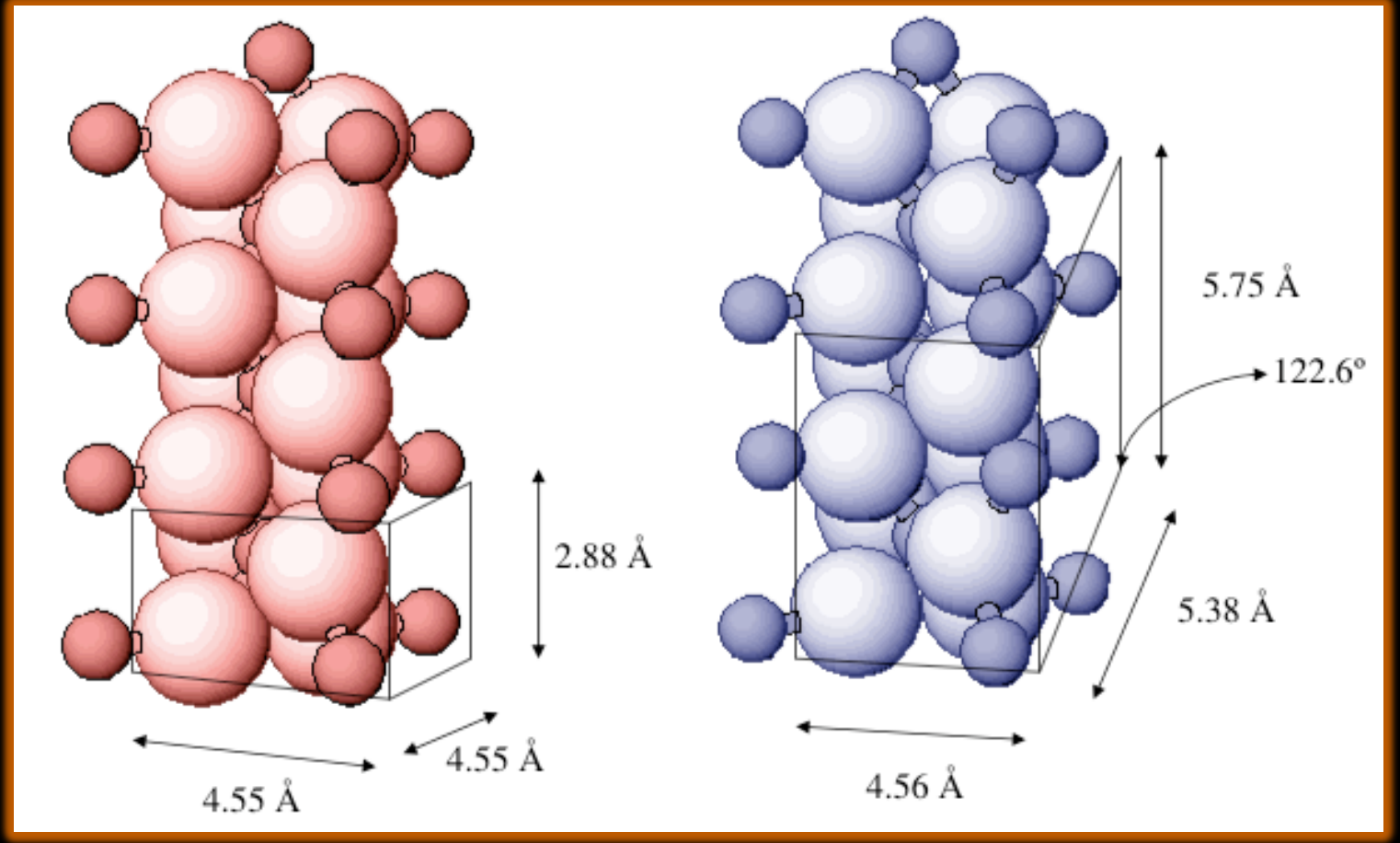
V4+

Free electrons

V-V $_{\text{dilatation}}$ ~Femto (V-V: 2.88Å)
Lattice expansion: ~Pico (V-V: 2.65Å, 3.12Å)

Baum, Zewail et al., Science 318 (5851), 788.

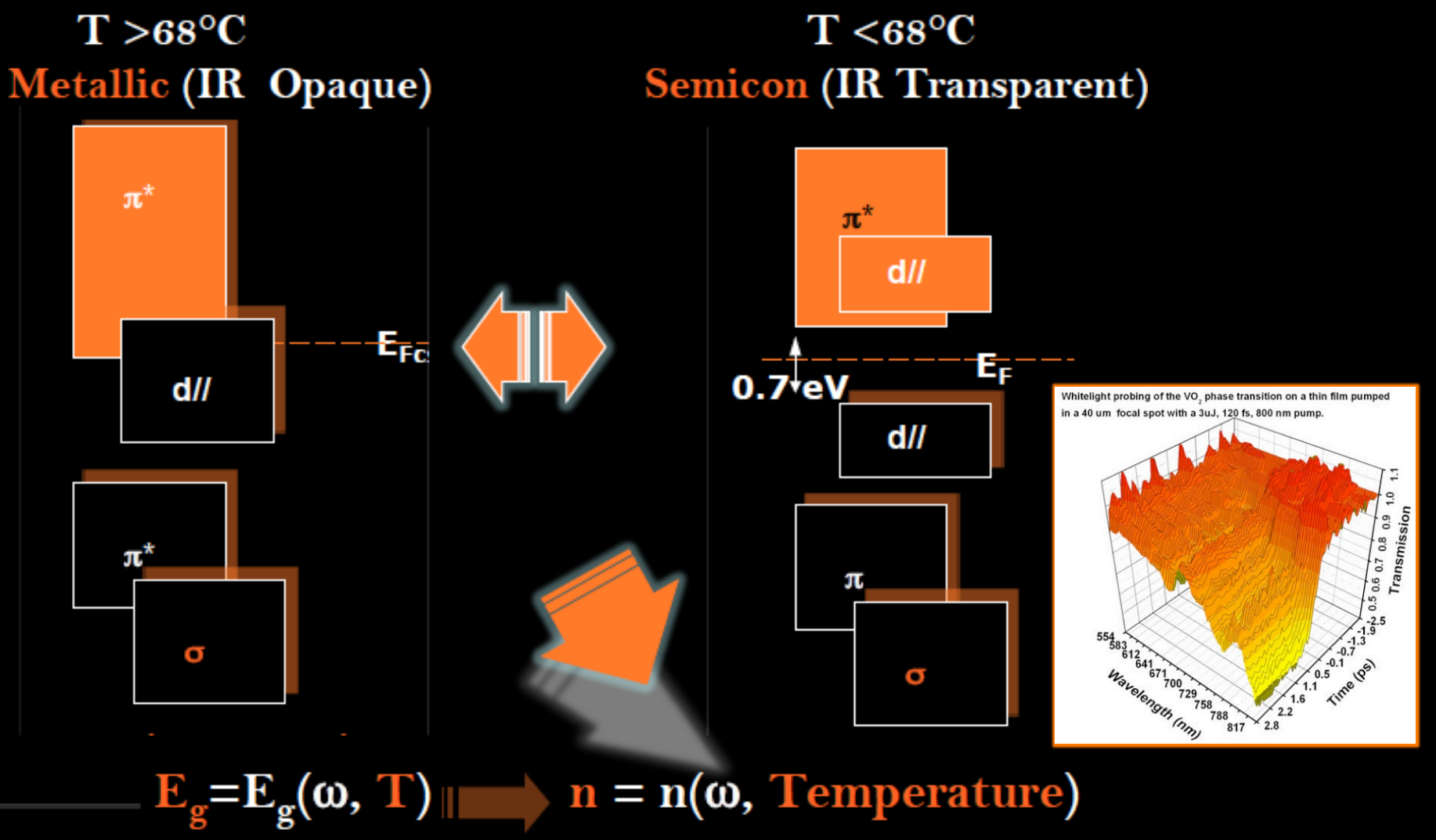
NANO: MOTT PHASE TRANSION
–Mott nano-scaled oxides



High T phase
Tetragonal (P_{42}/mnm)

Low T phase
Monoclinic (P_{21}/c)

NANO: MOTT PHASE TRANSION –Mott nano-scaled oxides



NANO: MOTT PHASE TRANSION

–Mott nano-scaled oxides

$$(n(\omega) + jk(\omega))^2 = \varepsilon_\infty + \varepsilon_1(\omega) + \varepsilon_2(\omega) + \varepsilon_3(\omega)$$

Lorentz comp. Semicon. state — **Drude comp Metallic state**

ε_∞ : **"Cte contribution due to high freq. electronic transitions"**

$$\varepsilon_1(\omega) = [(\varepsilon_s - \varepsilon_\infty)\omega_t^2]/[\omega_t^2 - j\omega\Gamma_0]$$

" ε_s: Static dielectric funct (ω=0),

$$\varepsilon_2(\omega) = \Sigma_{j=1}^{n}[f_j\omega_{0j}^2]/[\omega_{0j}^2 - \omega^2 + j\omega\gamma_i]$$

" ω_t , ω_{0j}^2: Resonant freq. of oscillators whose energies correspond to abs. peaks
" f_j : Oscillator strength "multiple Lorenz oscillators"
" Γ_0 , " γ_j : Broadening/ Damping factors

$$\varepsilon_3(\omega) = \omega_p^2 [-\omega^2 + j\omega\Gamma_d]$$

"Drude component"

NANO: MOTT PHASE TRANSION
–Mott nano-scaled oxides

$n = n(\omega, \text{Temperature})$

From Lorenz formula

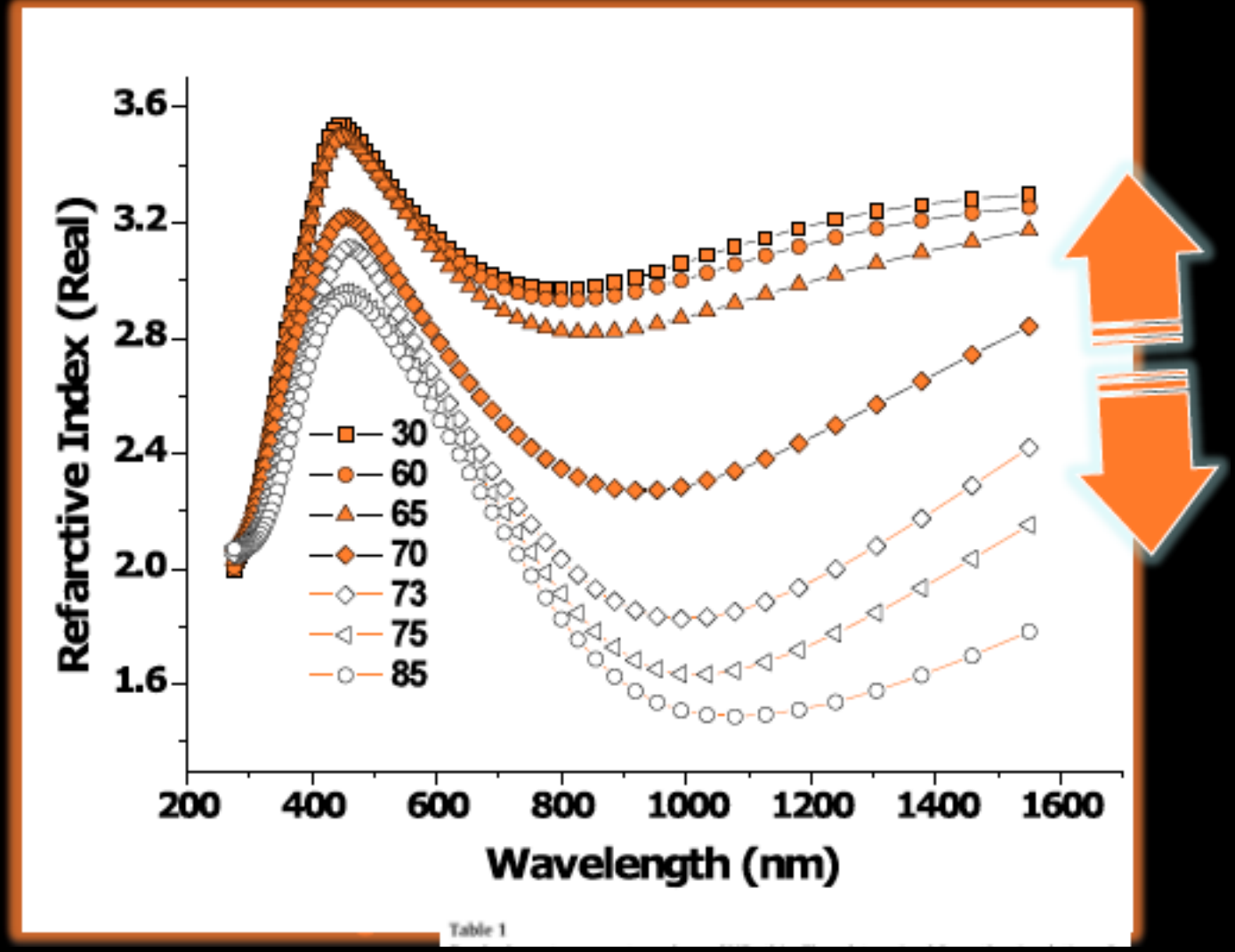
$$[n^2(T,\omega)-1]/[n^2(T,\omega)+2]=\rho(T)\alpha_\rho(\rho,T)/3\varepsilon_0$$

"ρ: Oscillator density"

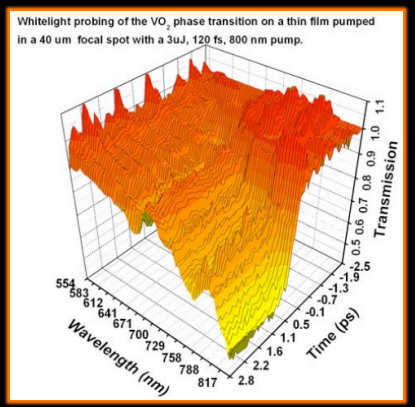
$$2n\varepsilon_0\, dn/dT=-[(n^2+2)(n^2-1)].\ \zeta(T)$$

$$\zeta(T)=\alpha_\rho[1-(V/\alpha_\rho)(\delta\alpha_\rho/\delta V)_T]+[(\delta\alpha_\rho/\delta T)_V/3\alpha_\rho]$$

NANO: MOTT PHASE TRANSION –Refractive index tunability

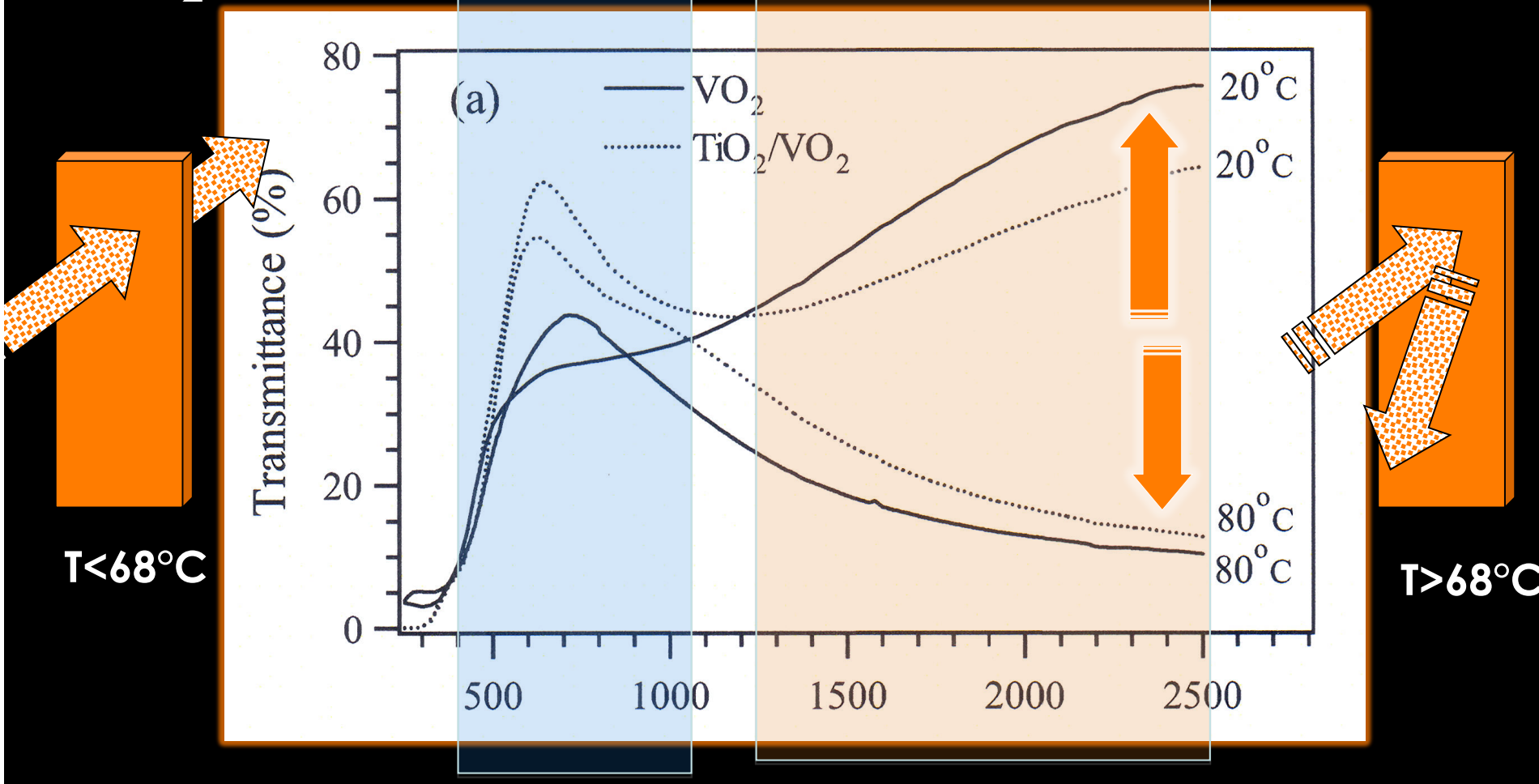


τ~180 fs



NANO: MOTT PHASE TRANSION

- VO_2 tunability & Smart Windows nano-Coatings

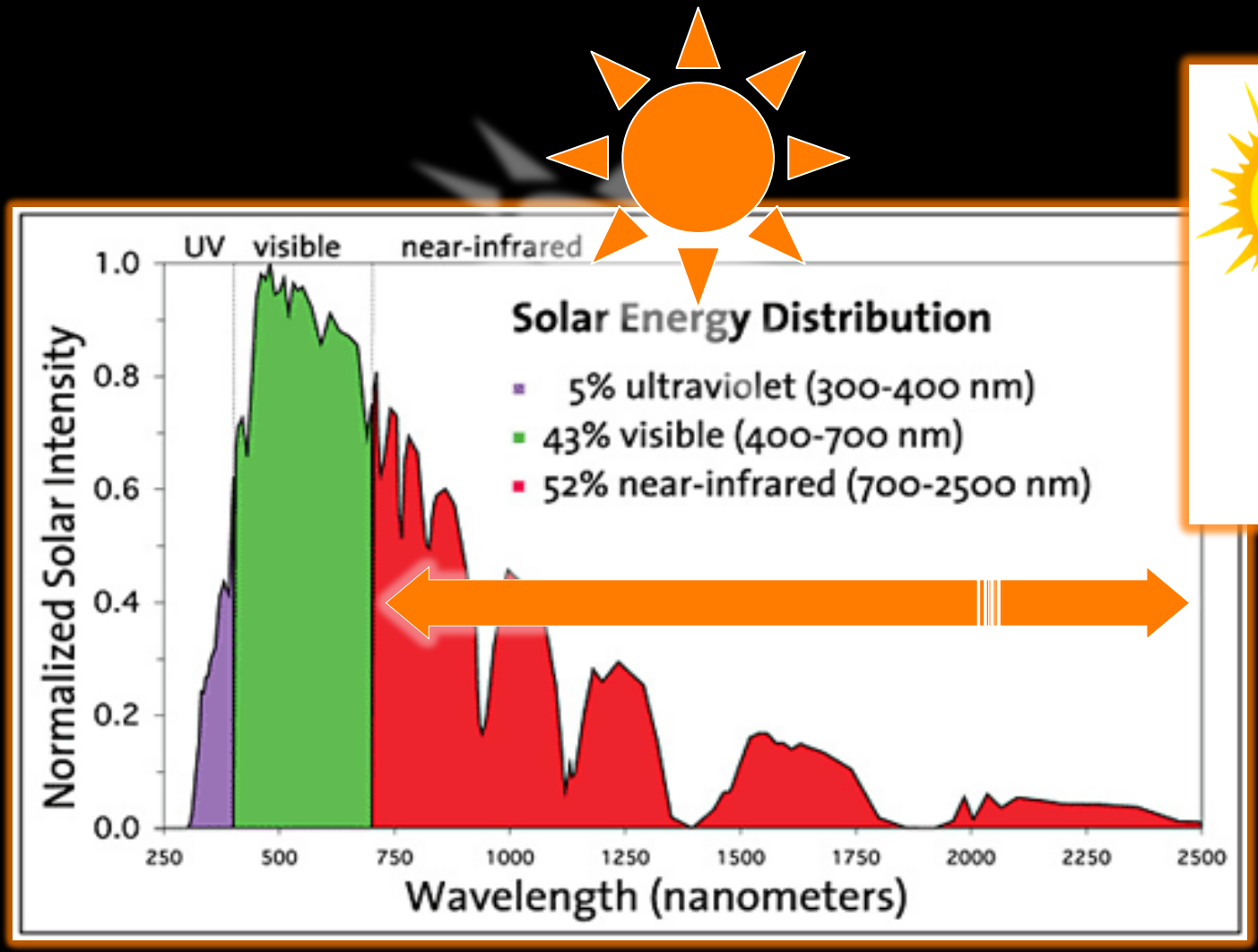


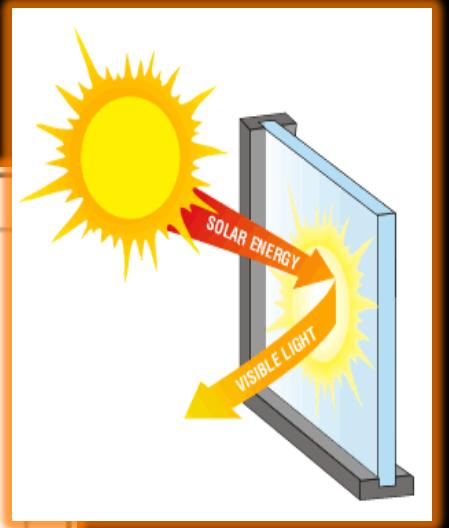
-Smart windows/air conditioning sector

-Vacuum based processing: Sputtering

NANO: MOTT PHASE TRANSION

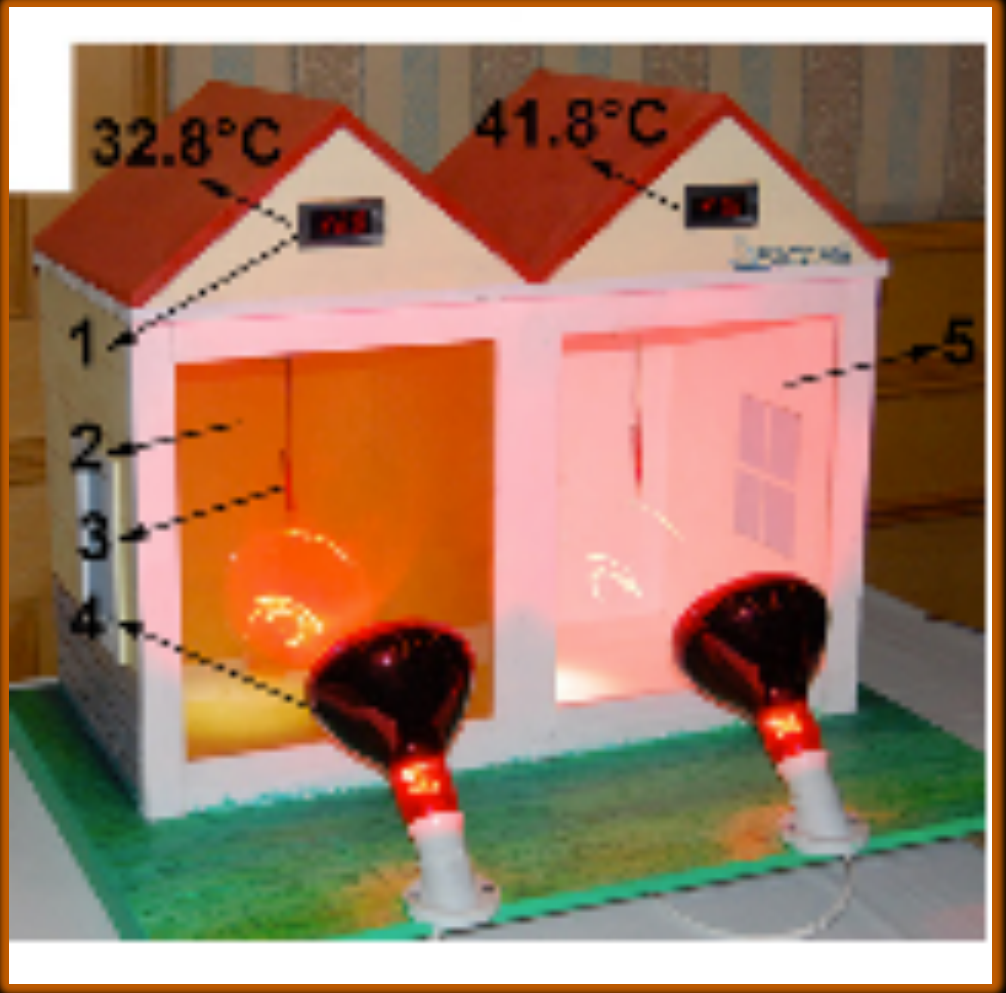
- VO_2 tunability & Smart Windows nano-Coatings

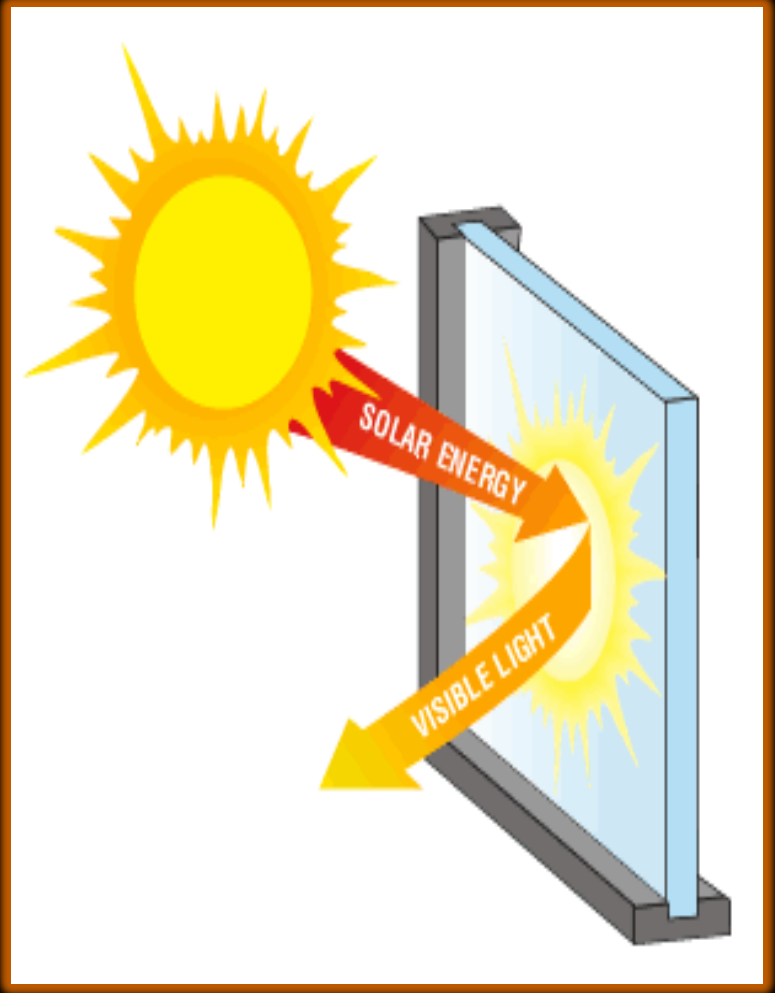




NANO: MOTT PHASE TRANSION

- VO_2 tunability & Smart Windows nano-Coatings



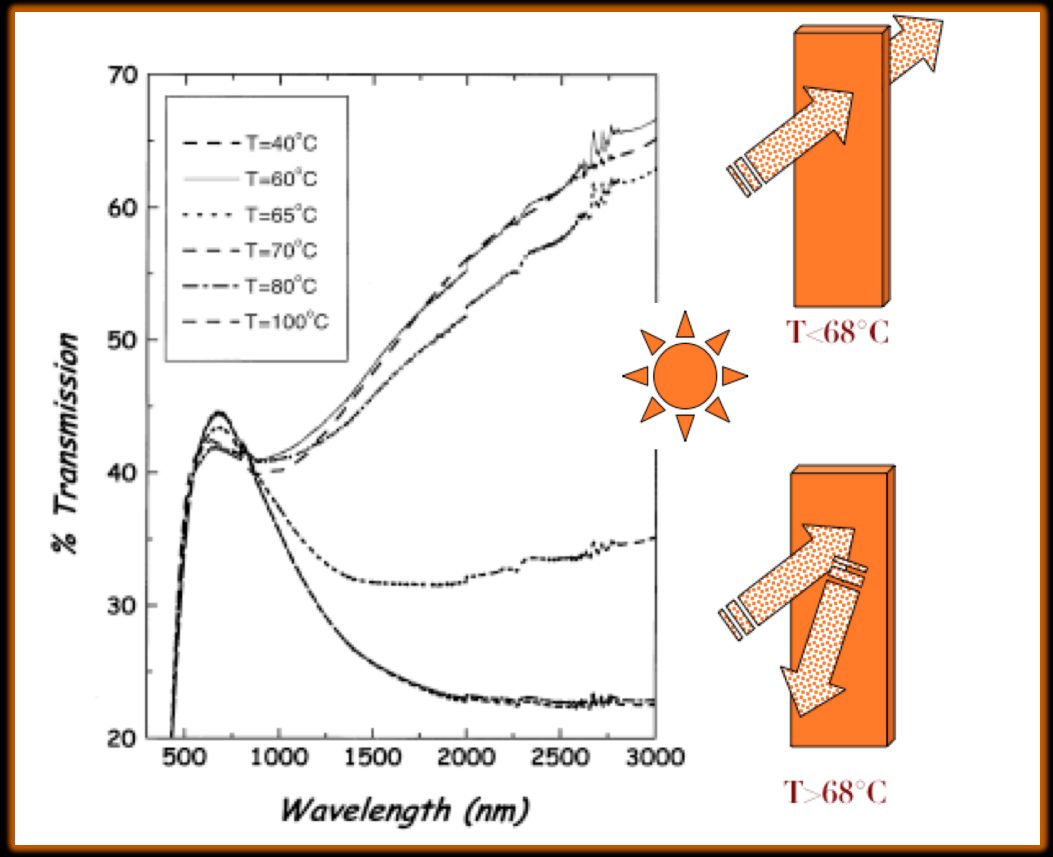


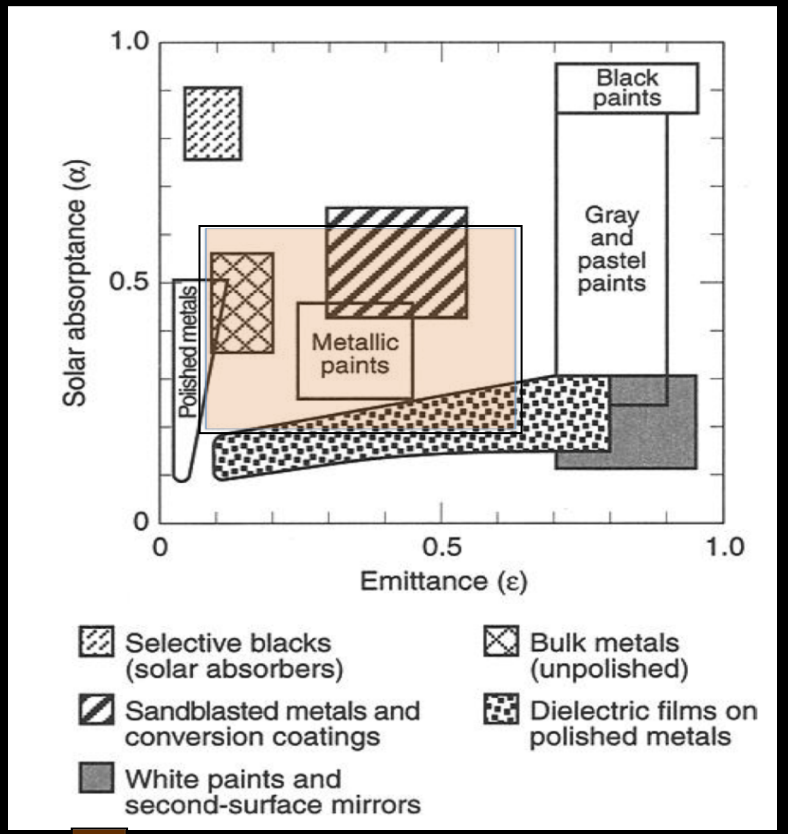
-Tuning down the Transition Temperaure: W/Mo doping

-Good T_{VIS} but not satisfactory ΔT_{IR}

NANO: MOTT PHASE TRANSION

- VO_2 tunability & Smart Windows nano-Coatings



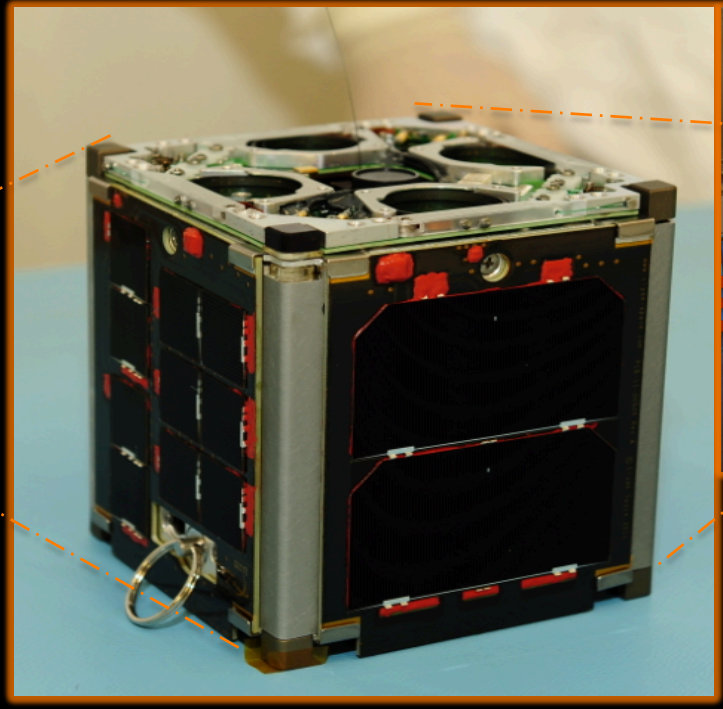


VO_2 based coatings

-Tuning the Emissivity ε(T): Space applications

NANO: MOTT PHASE TRANSITION

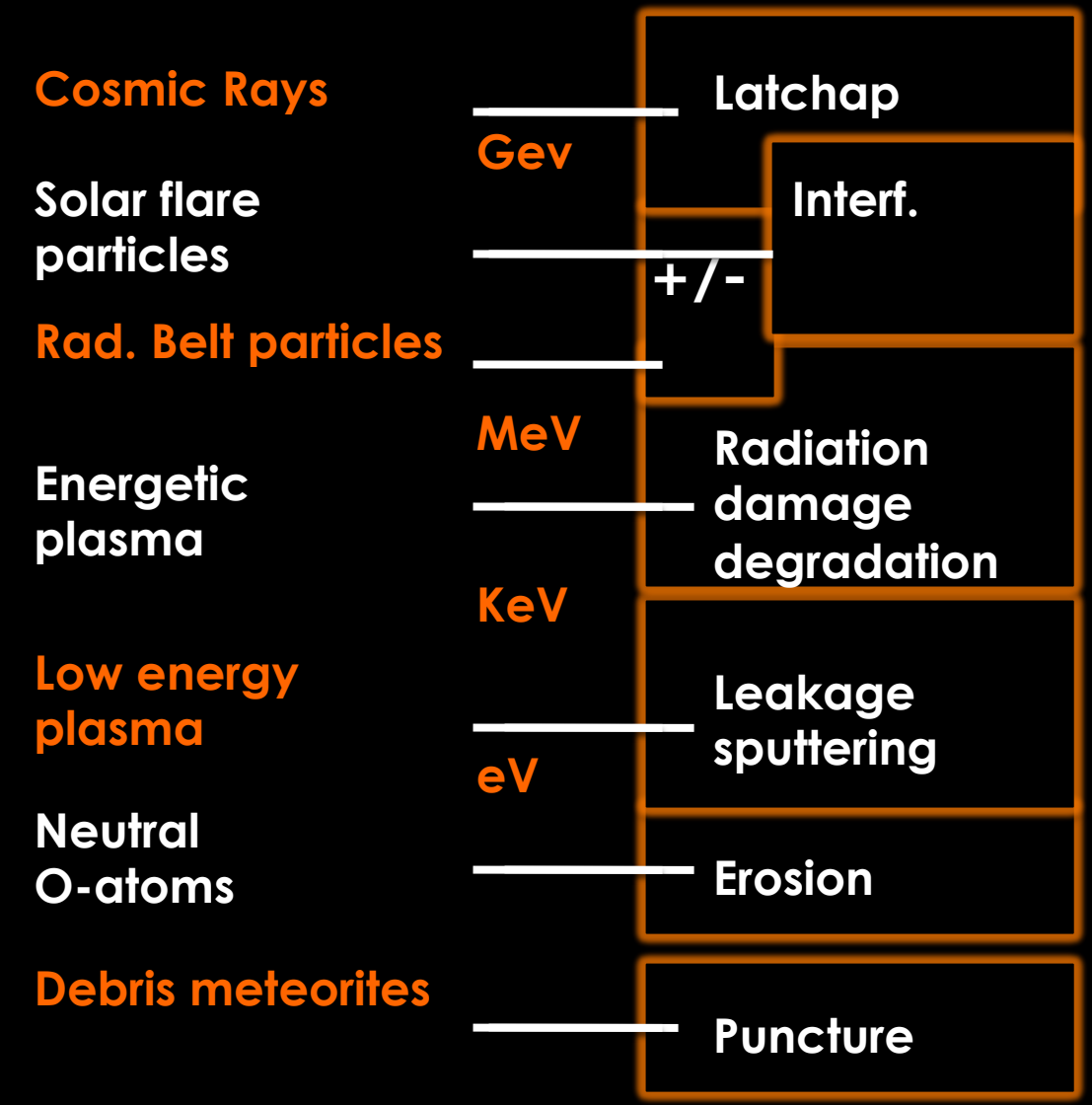
- VO_2 tunability & Nanosatellites



- **Multi-functionality: Heat control in small satelittes**
- **JAXA, ESA, Canadian Space Agency,**
- **SANSA: Sumbandilla: ≈ 81 kg/ZACube ≈ 1.175 kg**

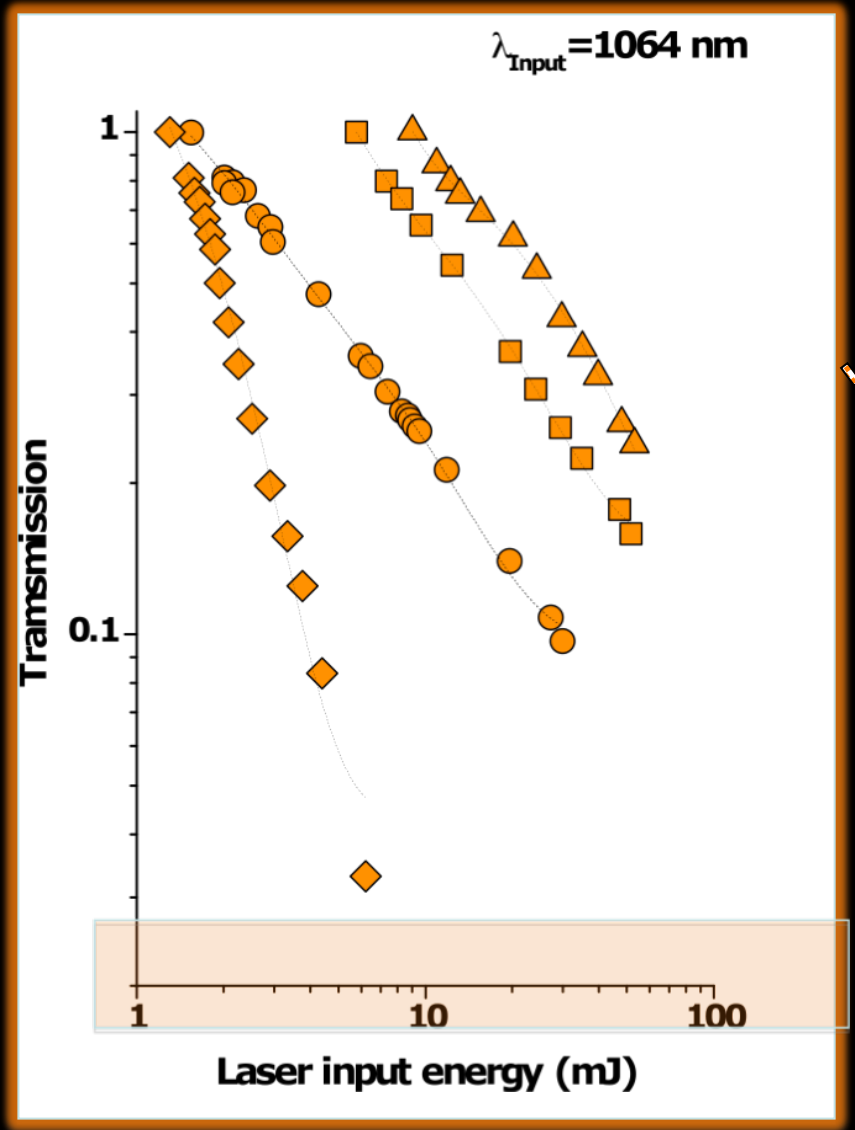
NANO: MOTT PHASE TRANSITION

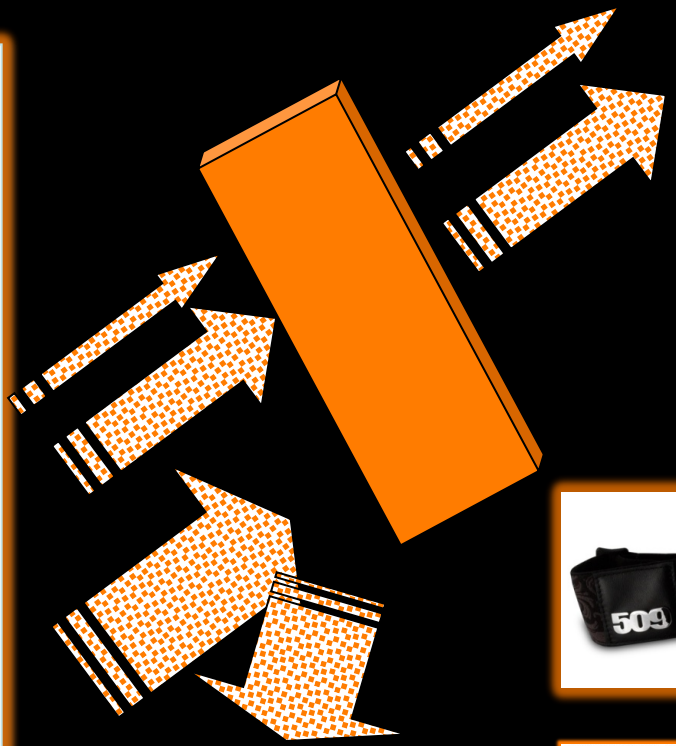
- VO_2 tunability & Nanosatellites

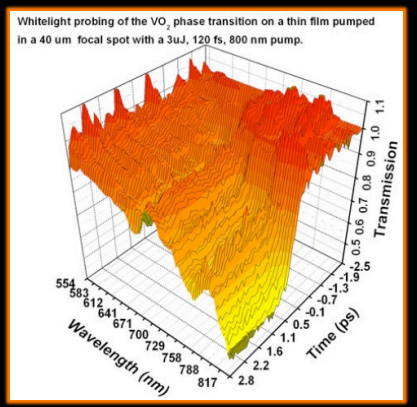


NANO: MOTT PHASE TRANSION

- VO_2 tunability & IR Optical Limiters





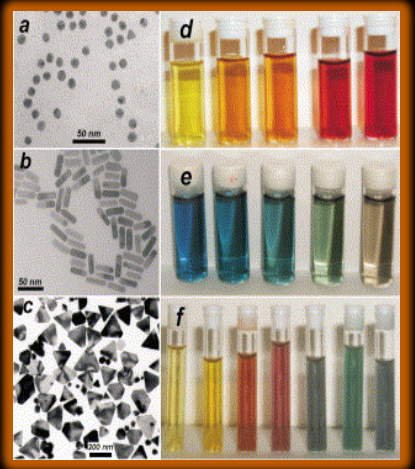


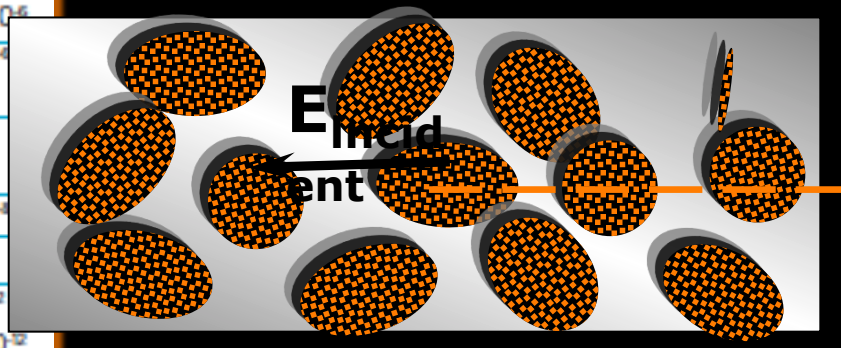
τ~180 fs

NANO: MOTT PHASE TRANSION

- VO_2 tunability & Tunable Femto nano-plasmonics

Diel.	Synth.	<ϕ/2> (nm)	% Au	λpr (nm)	λe (nm)	χeff (esu)
SiO_2	Co-Sput.	3.5-13	2-3	528 540	480 560	$1\ 10^{-7}$
SiO_2	ion-impl.	5-30	$4\text{-}7\ 10^{-2}$	-	532	$2\ 10^{-9}$
SiO_2	doped Glasses	1.4-15	1.10^{-5}	530 527	532	$8\ 10^{-14}$ $5.5\ 10^{-11}$
SiO_2	Co-Sput.	3-80	5-63	520 545	532	$2\ 10^{-9}$ $2.5\ 10^{-6}$
SiO_2	Co-Sput.	3	13-19	539	532	$-2.11\ 10^{-6}$
SiO_2	ion-impl.	2.9	7.9	525	532	$1.2\ 10^{-7}$
SiO_2	ion-impl.	1.5-3	1	505	532	$1.5\ 10^{-8}$
SiO_2	ion-impl.	5-25	5		532 591	$1.86\ 10^{-11}$ 2.93 10
Al_2O_3	Co-Sput.	10-250	25-60	545 590	532	1.2 10
TiO_2	Co-Sput.	10-250	15-60	630 670	532 670	$8\ 10^{-6}$ $6\ 10^{-7}$
Colloi.	Hydrosol	10	510^{-6}		530	1.5 10
Poly.	Organo.	24	7.210^{-3}	550		$1\ 10^{-8}$
Acet.		5-40	1.10-6	535	516 522	$-7\ 10^{-12}$ $-4.2\ 10^{-12}$

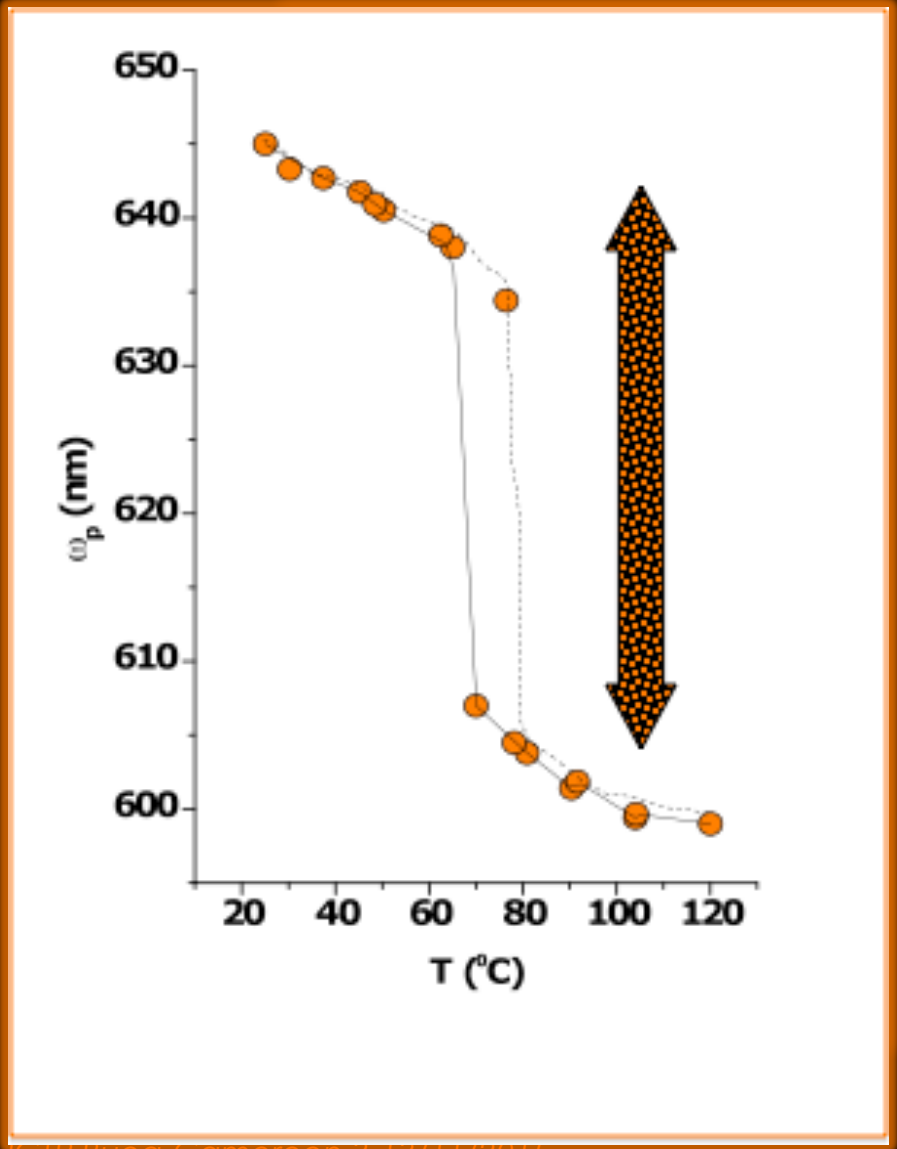


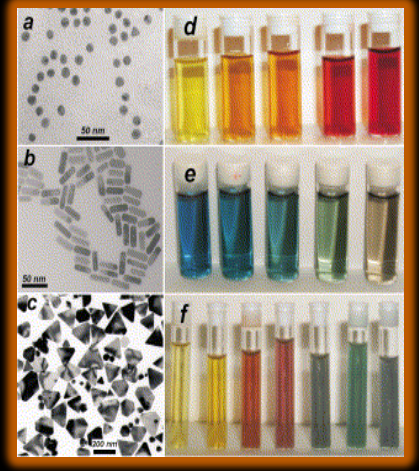


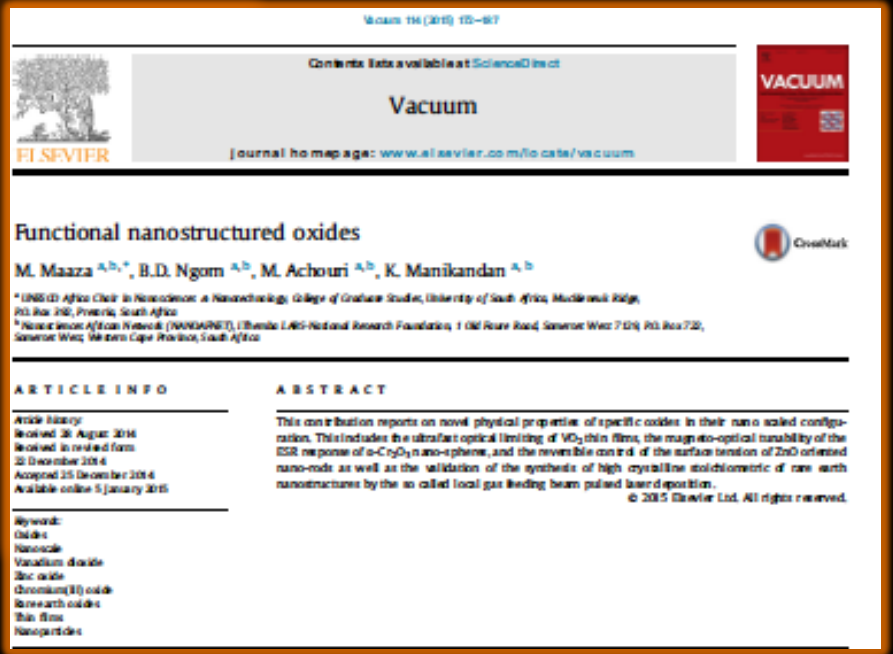
$$\omega_p^2 = (ne^2/e_m\ m_{eff})/(1+ 2\varepsilon_d(\omega,T))$$

NANO: MOTT PHASE TRANSION

- VO_2 tunability & Tunable Femto nano-plasmonics







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VACUUM

Functional nanostructured oxides

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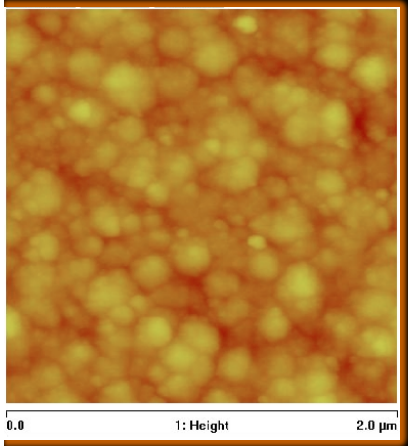
Nanoparticles

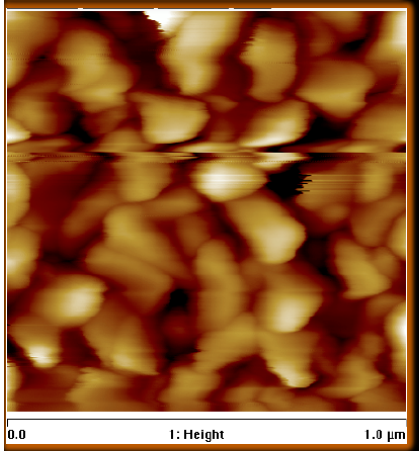
ABSTRACT

This contribution reports on novel physical properties of specific oxides in their nano scaled configuration. This includes the ultrafast optical limiting of VO_2 thin films, the magneto-optical tunability of the ESR response of α-Cr_2O_3 nano-spheres, and the reversible control of the surface tension of ZnO oriented nano-rods as well as the validation of the synthesis of high crystalline stoichiometric of rare earth nanostructures by the so called local gas feeding beam pulsed laser deposition.

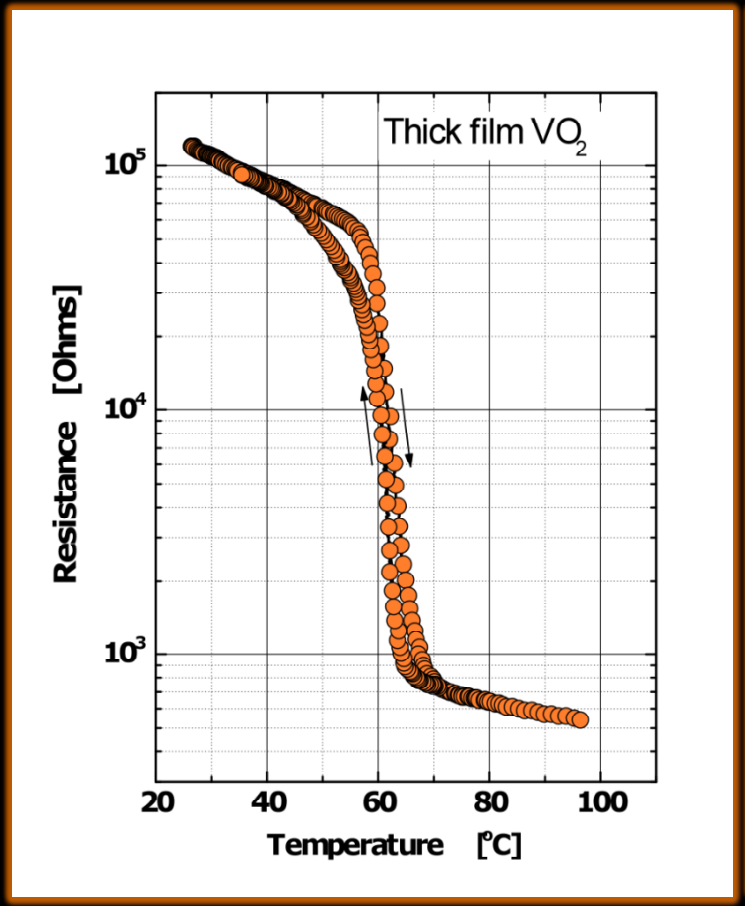
NANO: MOTT PHASE TRANSION

- VO_2 & Single nano-particle ultrafast gating

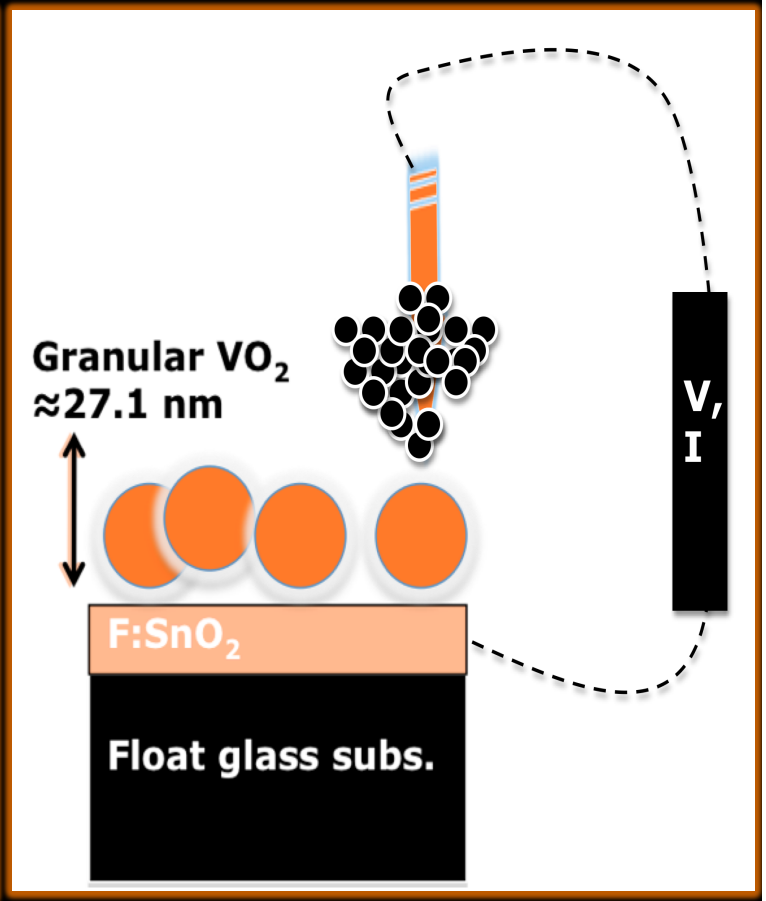




- Granular VO_2 film



- Thick VO_2 film

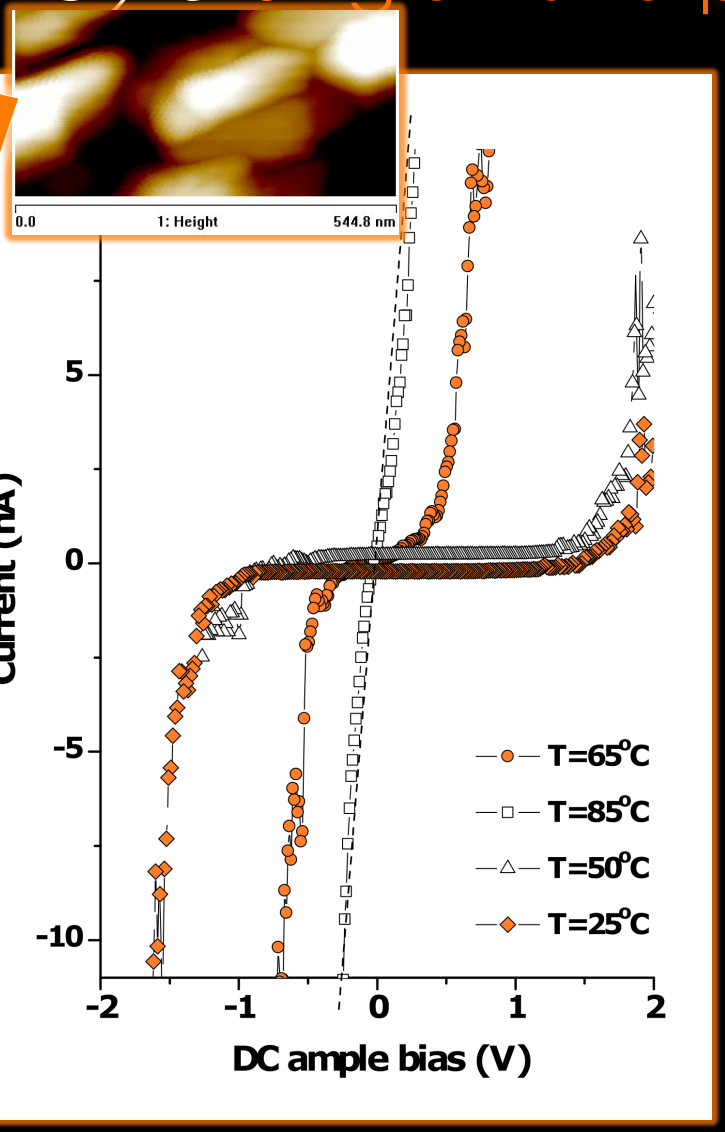


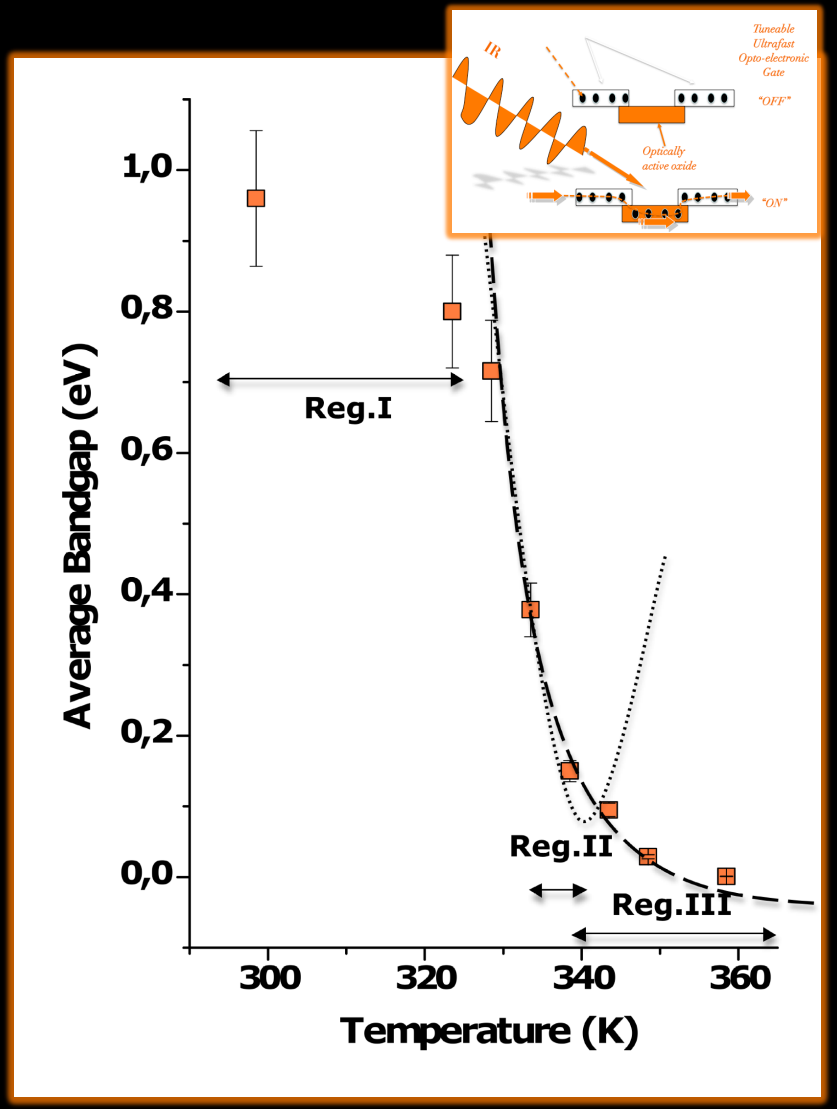
- STM set up

- **Mott phase transition in "Single nano-Grains"**
- **Possible Ultrafast & Tuneable VO_2 based gating**

NANO: MOTT PHASE TRANSION

- VO_2 & Single nano-particle ultrafast gating

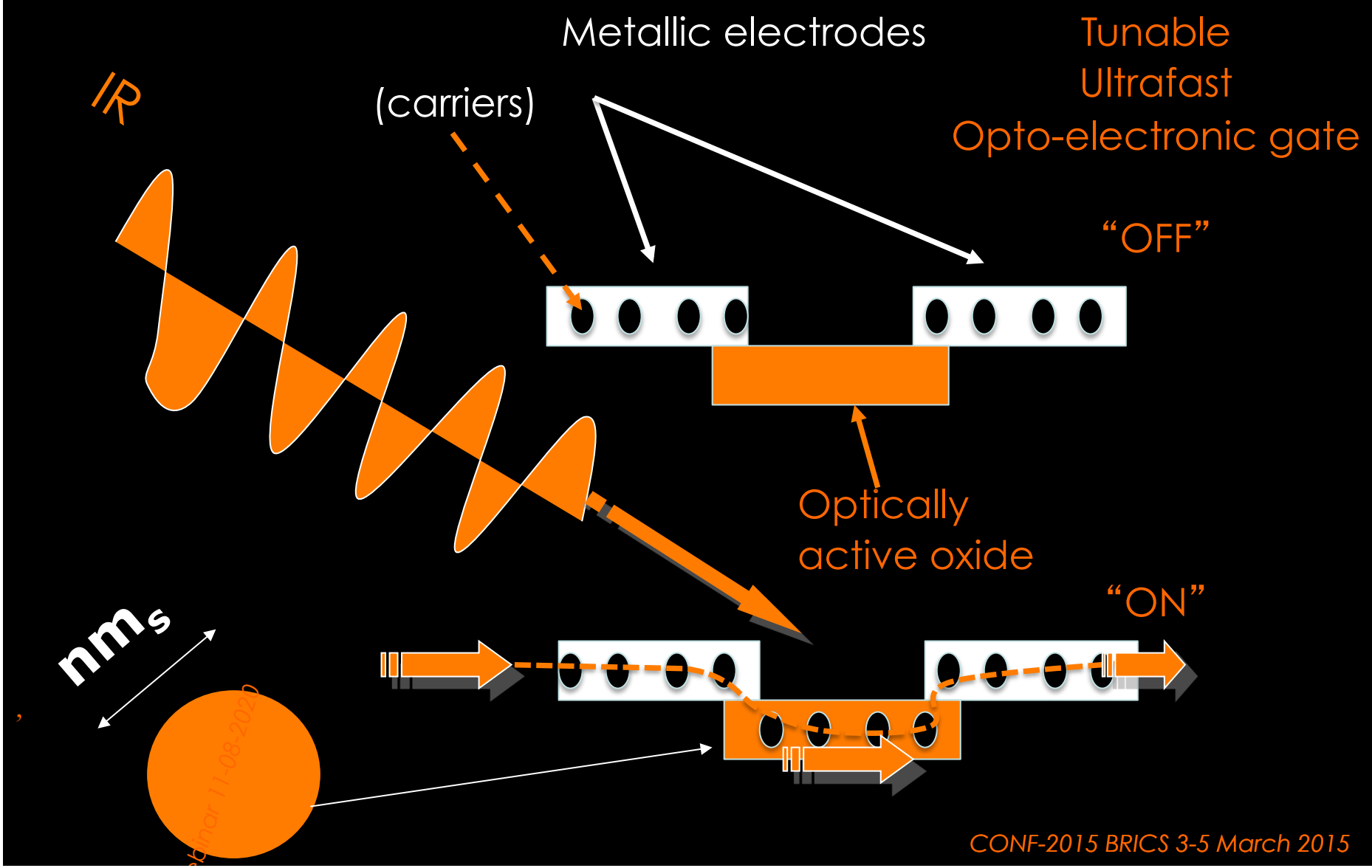




- **Proof of concept:** J. Nanoparticles Research (2014)

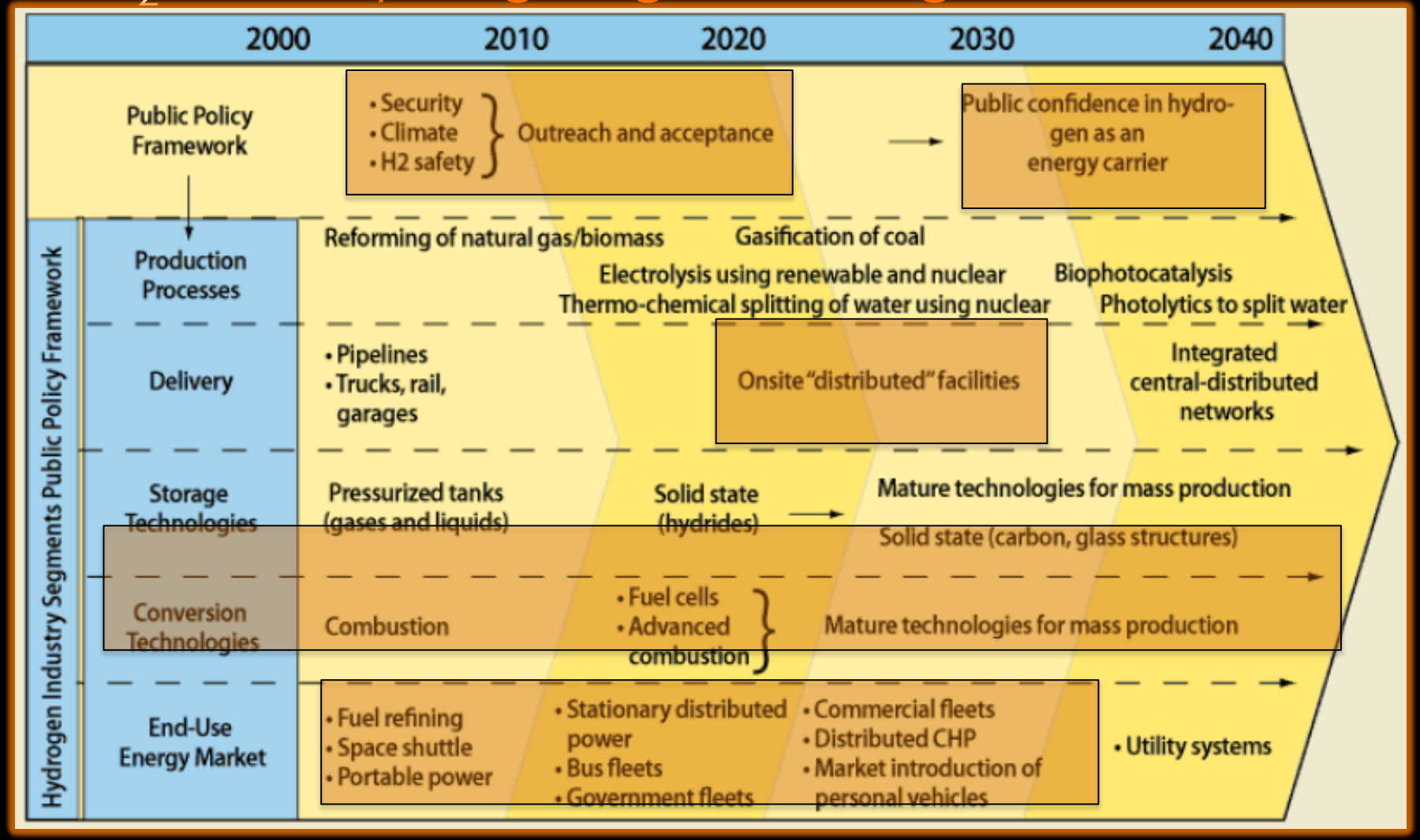
NANO: MOTT PHASE TRANSION

- VO_2 & Single nano-particle ultrafast gating



NANO: MOTT PHASE TRANSION

- VO_2 & RT Hydrogen gas sensing



Source: U.S. Department of Energy, 2005

NANO: MOTT PHASE TRANSION

- VO_2 & RT Hydrogen gas sensing

- [45] European Commission, Directorate for Energy and Transport, "Clean Urban Transportation for Europe: Detailed Summary of Achievements," http://ec.europa.eu/energy/res/fp6_projects/doc/hydrogen/deliverables/summary.pdf. (Last visited December 6, 2007.)
- [46] Green Car Congress, "European Commission Adopts 940M Fuel Cells and Hydrogen Joint Technology Initiative," www.greencarcongress.com/2007/10/european-commis.html. (Last visited November 16, 2007.)
- [47] Green Car Congress, "Japan Plans to Spend $1.72 Billion Over 5 Years to Spur Development of Low-Carbon Powertrains and Fuels," www.greencarcongress.com/2007/05/japan_plans_to_.html. (Last visited November 16, 2007.)
- [48] National Hydrogen Association, "Key Hydrogen Messages," p. 2, http://www.hydrogenassociation.org/pdf/keyHydrogenMessages.pdf. (Last visited November 14, 2007.)
- [49] U.S. Department of Energy, "U.S. Department of Energy Hydrogen Program," http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/doe_h2_program.pdf. (Last visited November 15, 2007.)

- [51] U.S. Department of Energy, *Fuel Cells and Infrastructure Technologies: Transition Strategies*, by Sig Gronich (Washington, D.C., March 8, 2006), http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/transition_wkshp_strategies2.pdf. (Last visited December 6, 2007.)
- [52] U.S. Department of Energy, *A National Vision of America's Transition to A Hydrogen Economy–to 2030 and Beyond* (Washington D.C. February 2002) p. iii, http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/vision_doc.pdf (last visited January 29, 2008.)

Transition to a Hydrogen Economy
Source: U.S. DoE 2006-8, FP5-6, MITI/MEXT-2007

NANO: MOTT PHASE TRANSION

- VO_2 & RT Hydrogen gas sensing

MAJOR REQUIREMENTS FOR A GAS SENSOR

- Sensitivity: Chemical Surface activity
- Operational Temperature: Low temp. functionality
- Detection threshold: Low threshold of detection
- Selectivity: Gas identification

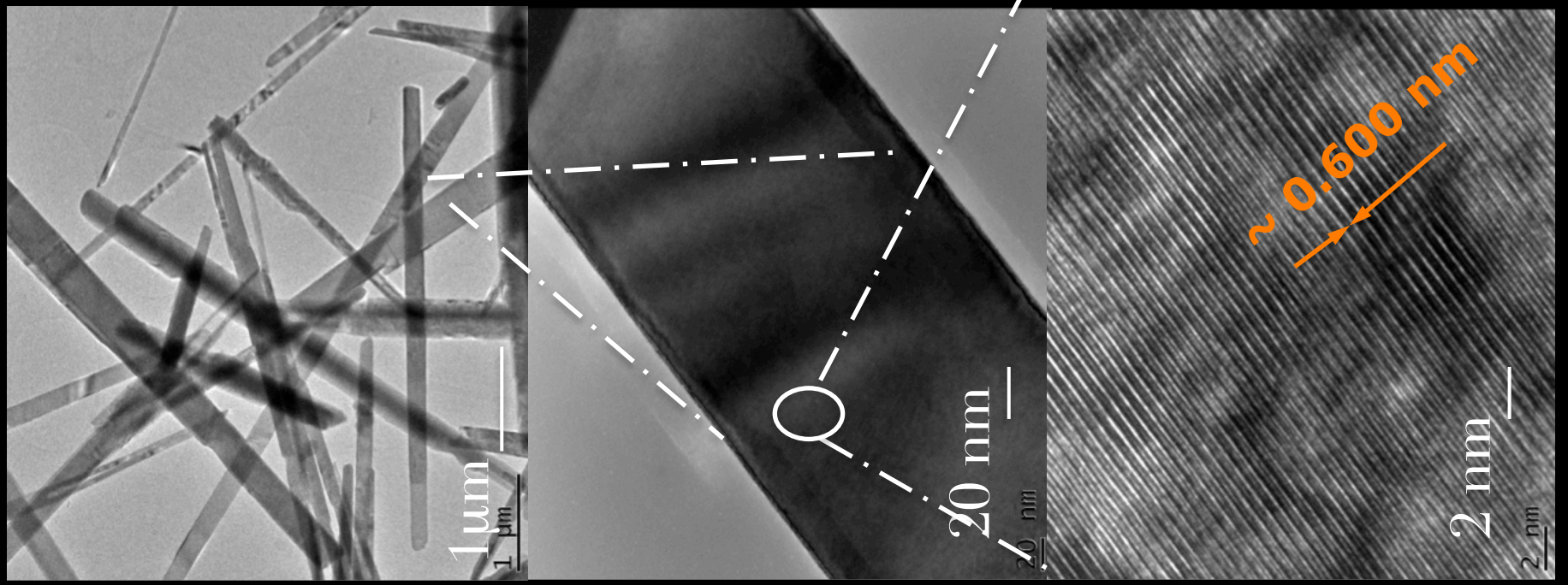
- *H_2: One of most explosive/ignition mix range with air of all gases with few exceptions; acetylene, silane, ethylene oxide.*
- *H_2: Odorless and leaks cannot be detected by smell.*

NANO: MOTT PHASE TRANSION

- VO_2 & RT Hydrogen gas sensing

Materials		Target Gas	Lowest detection Concentration	Response/Recovery
SnO_2	Nanowhiskers	Ethanol H_2	50 ppm (300 °C, S=23) 10 ppm (300, S=0.4)	N/A 10min N/A
	Single nanowire	H_2 Humidity	100 ppm (2, S=13) RH:30% (30°C,S≈1.25)	N/A 120-170s/20-60s
	Nanorods	H_2	100ppm (150 °C)	N/A
In_2O_3	Nanowires	Ethanol	100ppm (370 °C, S≈2)	10s/~20s
		NO_2	1ppm (250 °C, S≈2.57)	N/A
		H_2S	200ppb (RT)	2-3min/N/A
		Ethanol	5ppm (330 °C, S≈1.84)	6s/11s
	Single NW	H_2S	1ppm (120 °C)	48s/56s
ZnO	Nanorods	H_2	500ppm (25 °C)	10min/ N/A
		H_2S	50ppb (RT, S≈1.7)	N/A
		Ethanol	1ppb (300°C, S≈10)	N/A
		Methanol	50ppm (300 °C, S≈3.2)	N/A
		Ethanol	100ppm (325°C, S≈20)	N/A
	Single NW	H_2	200ppm (RT, S≈0.04)	
WO_3 nanowires		H_2S	1ppm (250°C, S≈48)	N/A
		NH_3	10ppb(room temp.)	N/A
TeO_2 nanowires		NO_2	10ppm (26 °C)	10min
		NH_3	10ppm (26 °C)	> 30min
		H_2S	50ppm (26 °C)	N/A
CuO	nanowires	CO	30ppm (300 °C,	N/A
		NO_2	S≈0.07) 2ppm (300 °C, S≈0.15)	N/A
	nanoribbons	Methanol	5ppm (100 °C, S≈1.4)	2-4s/3-7s
		Ethanol	5ppm (200°C, S≈1.2)	3-6s/4-9s
CdO nanowires		NO_2	1ppm (100 °C, S≈0.27)	N/A

NANO: MOTT PHASE TRANSION –Mott nano-scaled oxides

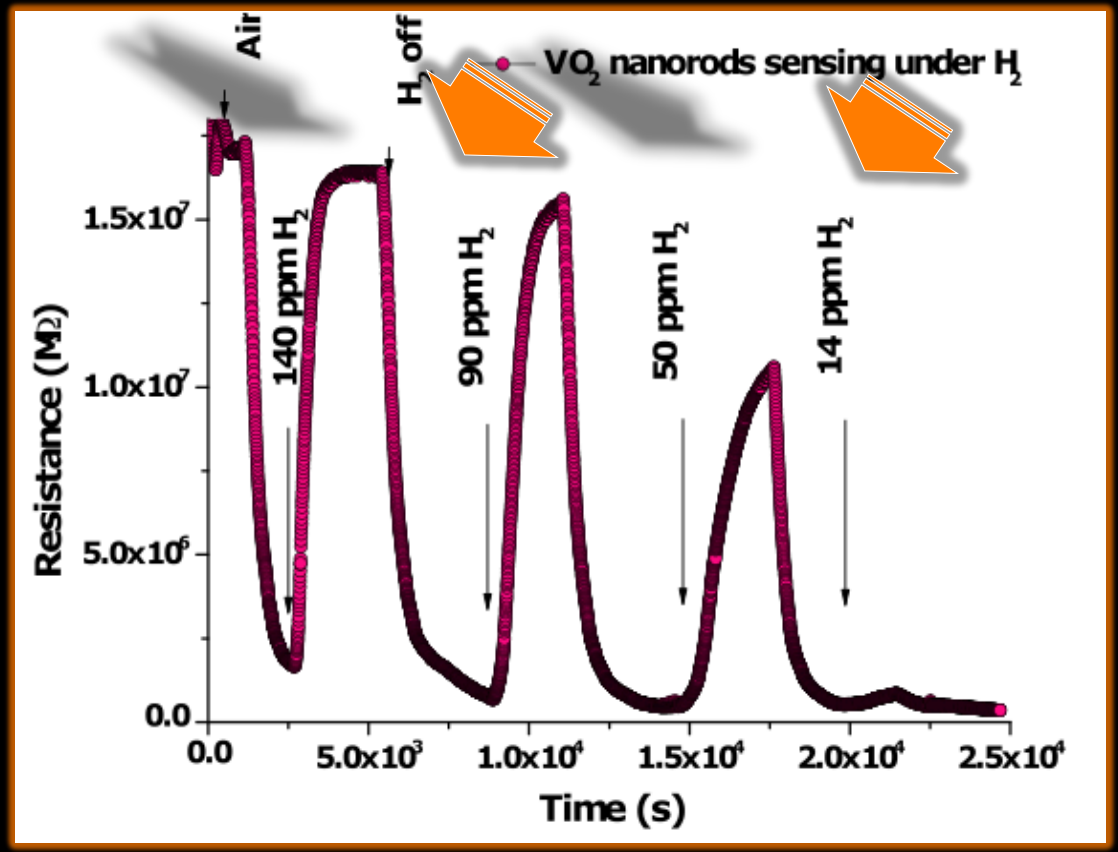


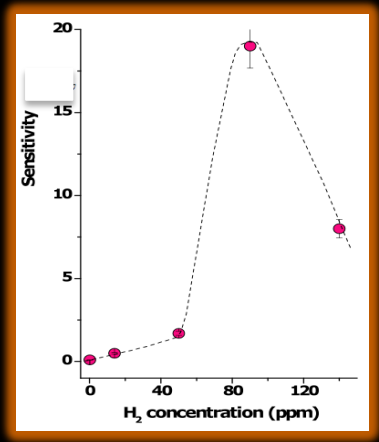
- Nanobelts: 20-150 nm in the transversal direction & a length ≥ 20 μ m with a thickness less than 10 nm.
- VO_2 (A): specific interspacing $d_{(011)}$~ 0.600 nm.

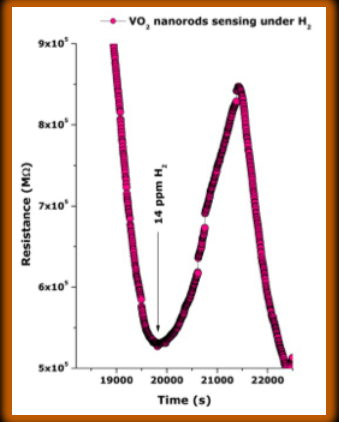
NANO: MOTT PHASE TRANSION

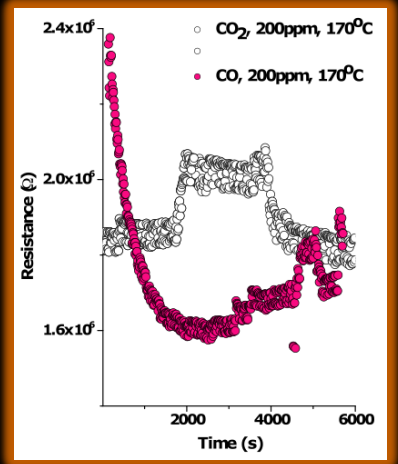
–Mott nano-scaled oxides

- Different H_2 partial pressures equivalent to 140, 90, 50, 14, 0.17 ppm of H_2 (N_2 carrier): Standard gas sensing BUT at RT.
- Average response time are ~840, 890, 1080, 1020, 1050s for 140, 90, 50, 14 and 0.17 ppm of H_2respectively.









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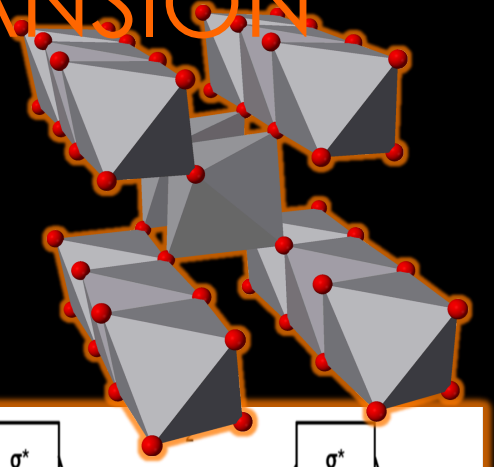
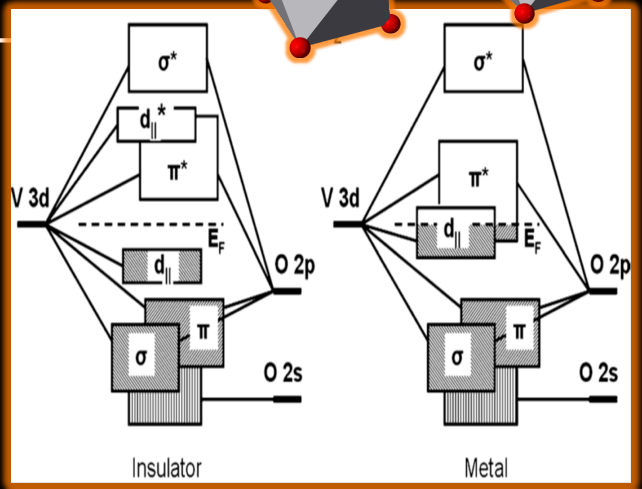


MULTI-VALENCE OXIDES: VO_2

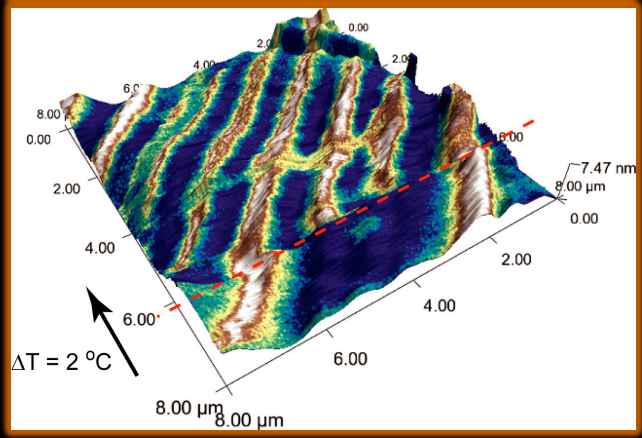
Phase Diagram

- V has abundant oxidation states: 0,…
- Large binary : VO_{2+x} ($-0.5 \leq x \leq 0.5$),
- V_2O_5, V_3O_7, V_4O_9, V_6O_{13}, VO_2, V_2O_3,



VO_2:

- Polymorphic system
- VO_2 (A), VO_2 (B), VO_2 (M), VO_2 (R)
- Active/non active phases.
- Stress controlled
- VO_2(M-R)



NANO: MOTT PHASE TRANSION –Mott nano-scaled oxides

The O-V (Oxygen-Vanadium) System*

By H.A. Wriedt
Consultant

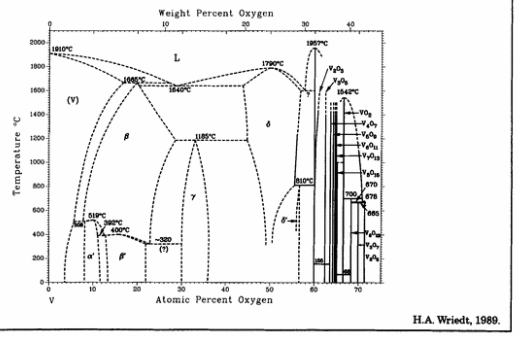
Equilibrium Diagram

The equilibrium solid phases of the V-O system at 0.1 MPa hydrostatic pressure are (1) the bcc terminal solid solution, (V); (2) bct α'; (3) bct β; (4) bct β'; (5) monoclinic γ; (6) fcc δ; (7) bct δ'; (8) V_2O_3, with rhombohedral and monoclinic forms above and below –112 °C; (9) V_3O_5, with different monoclinic forms above and below +155 °C; (10) the triclinic V_nO_{2n-1} Magnéli series, with n = 4, 5, 6, 7, and 8; (11) VO_2, with tetragonal β and monoclinic α forms above and below + 68 °C; (12) V_6O_{13}, with different monoclinic forms above and below –124 °C; (13) monoclinic V_3O_7; and (14) orthorhombic V_2O_5. Numerous alternative designations to those adopted occur in the literature. Most solid phases exhibit detectable composition ranges, except for V_3O_5, the Magnéli phases, V_6O_{13}, and V_3O_7, where the breadths are on the order of the experimental uncertainties. The ranges in VO_2 and V_2O_5 are also very narrow. Among the many other phases reported, most are either unconfirmed or demonstrably unstable. The established phases V_9O_{17} and V_4O_9 might be marginally stable, but they are omitted from the assessed V-O phase diagram (Fig. 1).

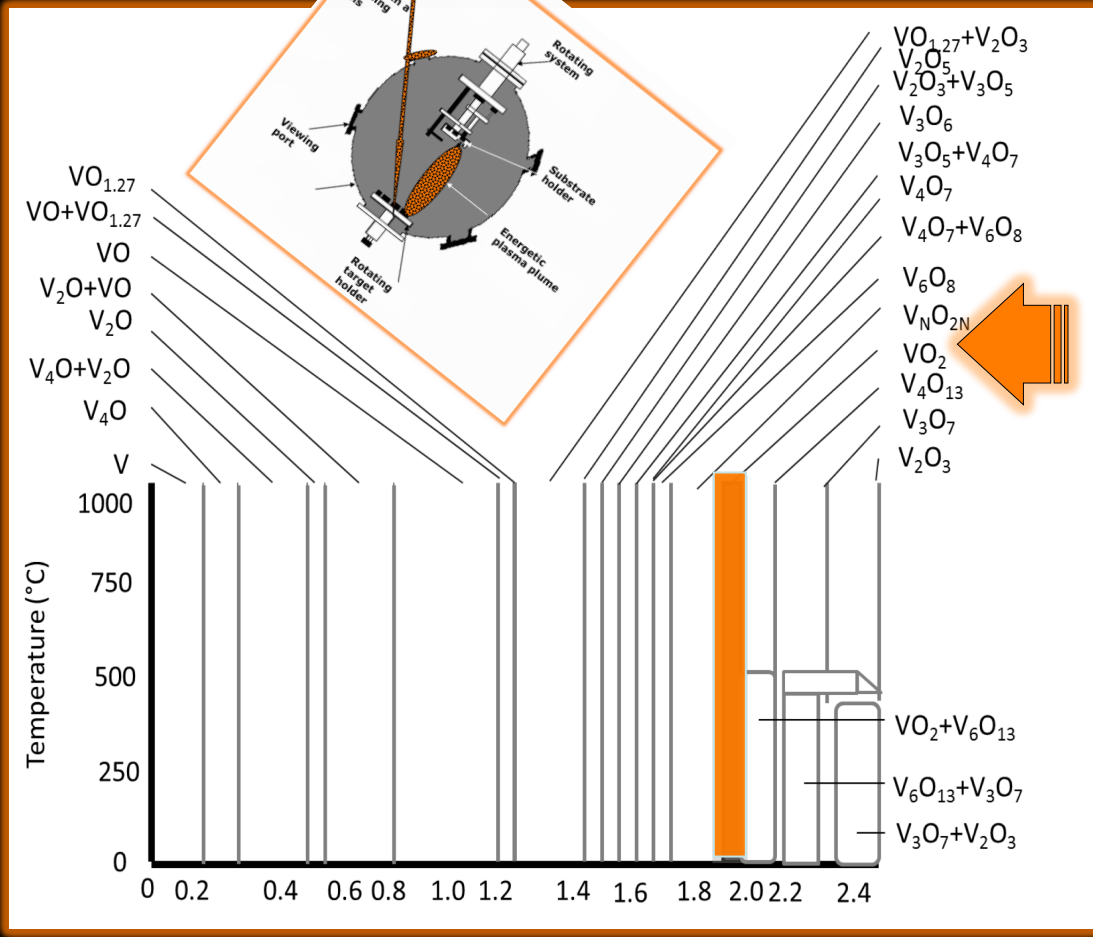
The pioneer draftings of the V-O phase diagram—[53Sey] and [57Bur] below and above 60 at.% O, respectively—incorporated both long-known and then recently discovered phases: (V), β, δ, V_2O_3, V_3O_5, V_nO_{2n-1} Magnéli, VO_2, V_6O_{13}, and V_2O_5. Major revisions followed. Phases were deleted ("γ" of [53Sey]) or added by [55Ros] (γ), by [66Tod] (V_3O_7, discovered by [65Tud]), by [70Hen] (α', discovered by [69Cam]), by [71Bel] (δ', discovered by [42Kle]), and by [74Hir] (β', discovered by [73Hir]). The phase relationships and invariant equilibria depicted in the assessed diagram (Fig. 1), which incorporates all of these phases, were derived primarily below 55 at.% O from the diagram of [71Ale] (modified by detail from [71Bel] and [75Hir2]) and above 67 at.% O from [66Tod] (modified by detail from [80Vas]). Between 55 and 67 at.% O, the main influence was the [66Kac] diagram. Table 1 lists the known phase transformations and invariant equilibria.

*Unabridged version of this assessment can be found in *Phase Diagrams of Binary Vanadium Alloys*, Monograph Series on Alloy Phase Diagrams, by J.F. Smith, published by ASM INTERNATIONAL, July 1989.

Fig. 1 Assessed V-O Phase Diagram (Condensed System, 0.1 MPa)



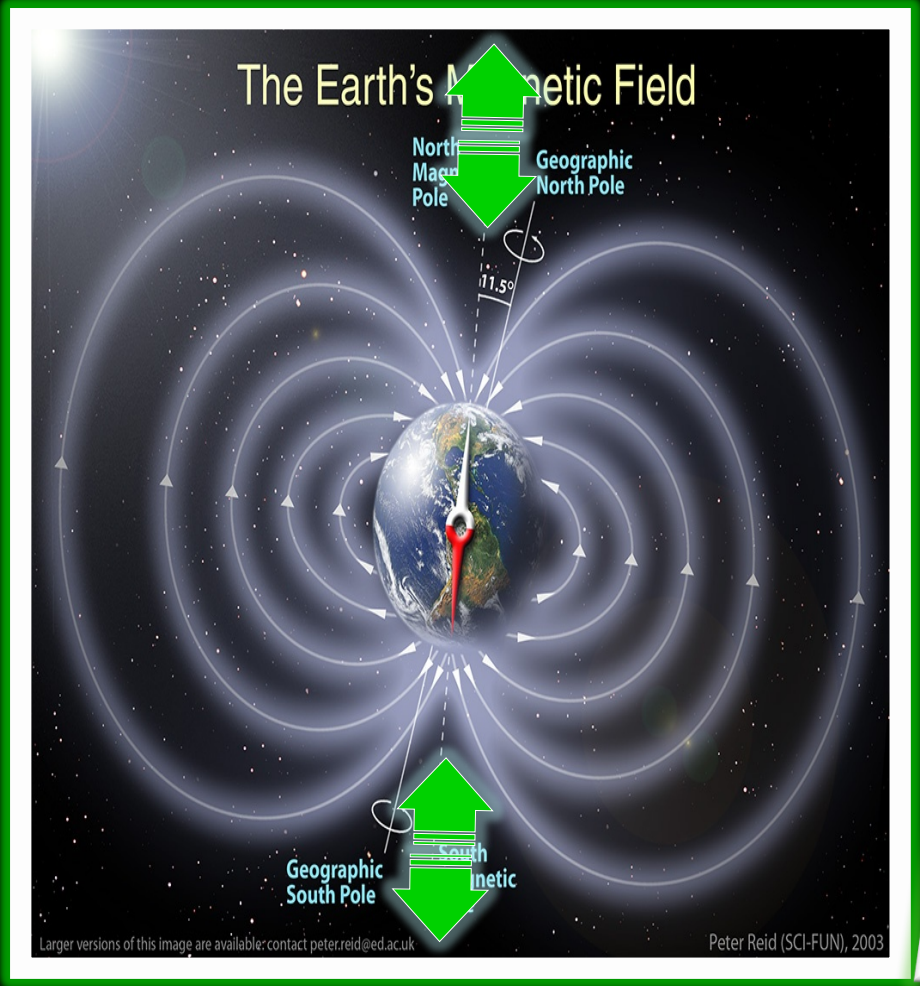
H.A. Wriedt, 1989.

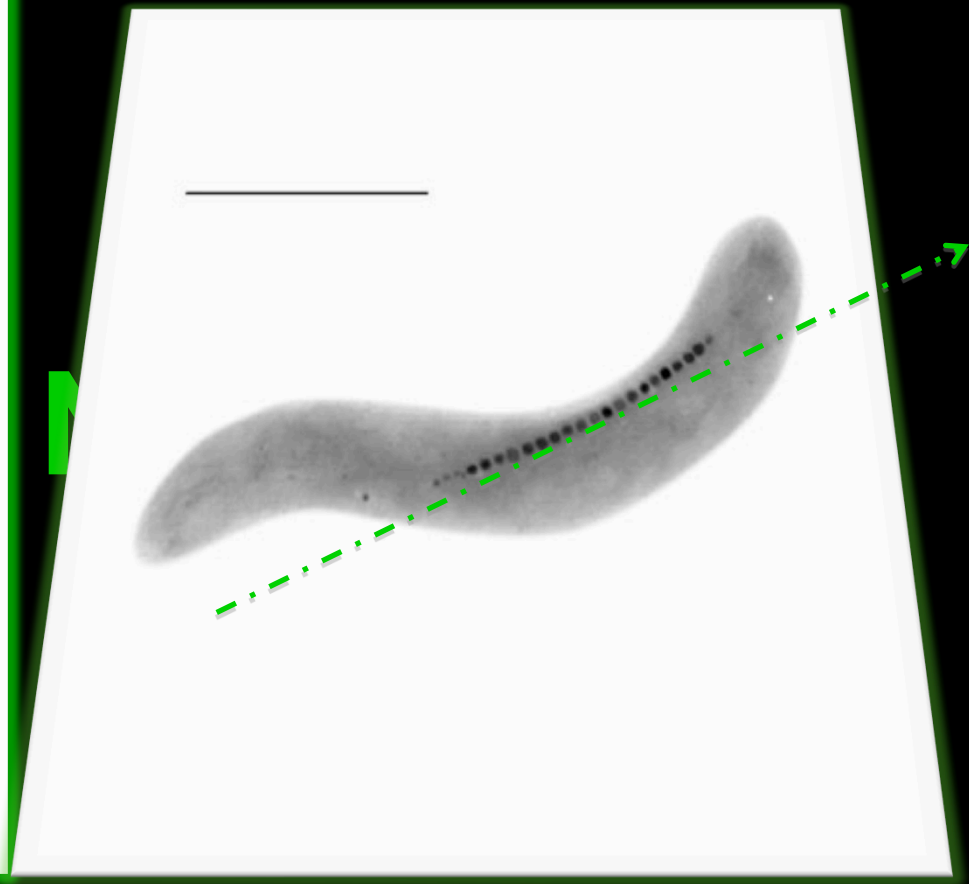


- V-O has abundant crystallographic states
- VO_2Narrow P-T-% range: Challenging synthesis
- Targeted VO_2 M-R active phase: PLD

NANO-3:
NANO IN NATURE

NANO IN NATURE: NATURAL NANO-FACTORIES



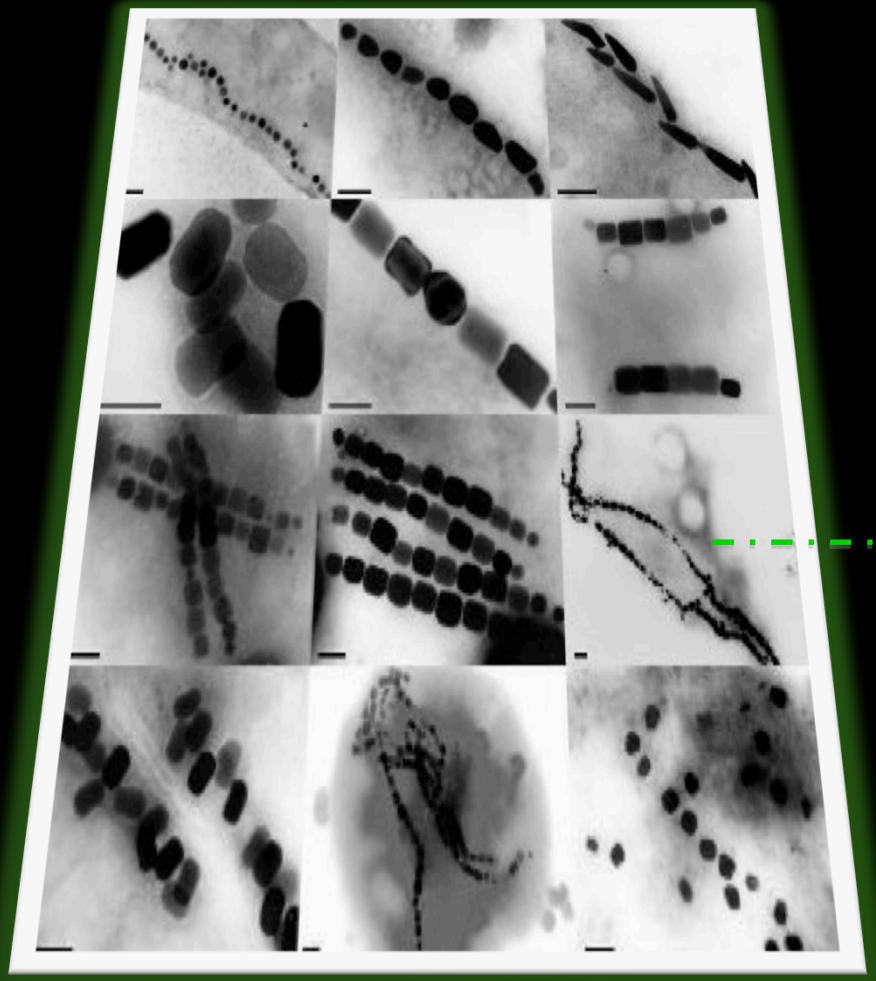


Magnetostatic Bacteria

-Marine Spirillum Strain MV4

ASP-CERN Webinar 11-08-2020

NANO IN NATURE: NATURAL NANO-FACTORIES



50 nm

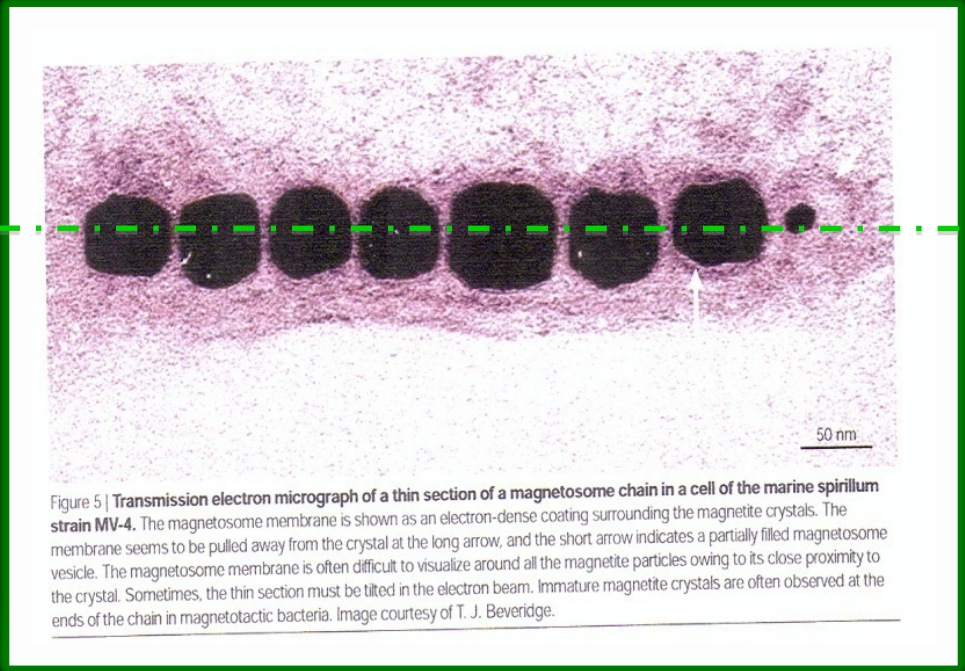


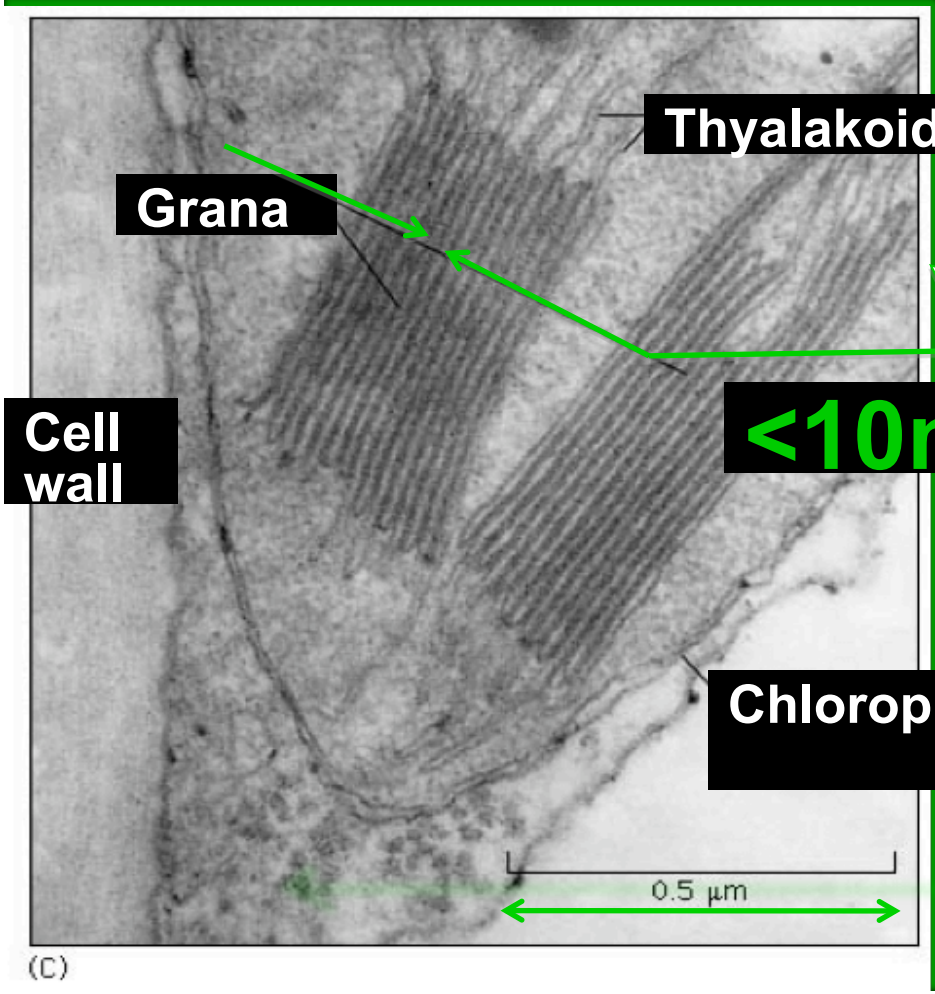
Figure 5 | **Transmission electron micrograph of a thin section of a magnetosome chain in a cell of the marine spirillum strain MV-4.** The magnetosome membrane is shown as an electron-dense coating surrounding the magnetite crystals. The membrane seems to be pulled away from the crystal at the long arrow, and the short arrow indicates a partially filled magnetosome vesicle. The magnetosome membrane is often difficult to visualize around all the magnetite particles owing to its close proximity to the crystal. Sometimes, the thin section must be tilted in the electron beam. Immature magnetite crystals are often observed at the ends of the chain in magnetotactic bacteria. Image courtesy of T. J. Beveridge.

Magnetostatic Bacteria
-(100) FeS_2 or (111) Fe_3O_4 nano-crystals

NANO IN NATURE: NAT. PHOTOSYNTHESIS

Photon Absorption — Photo Chemistry — e-Transport — Biochemistry — Physiology

fs — ps — ns — ms — ms-s — >>> 1s

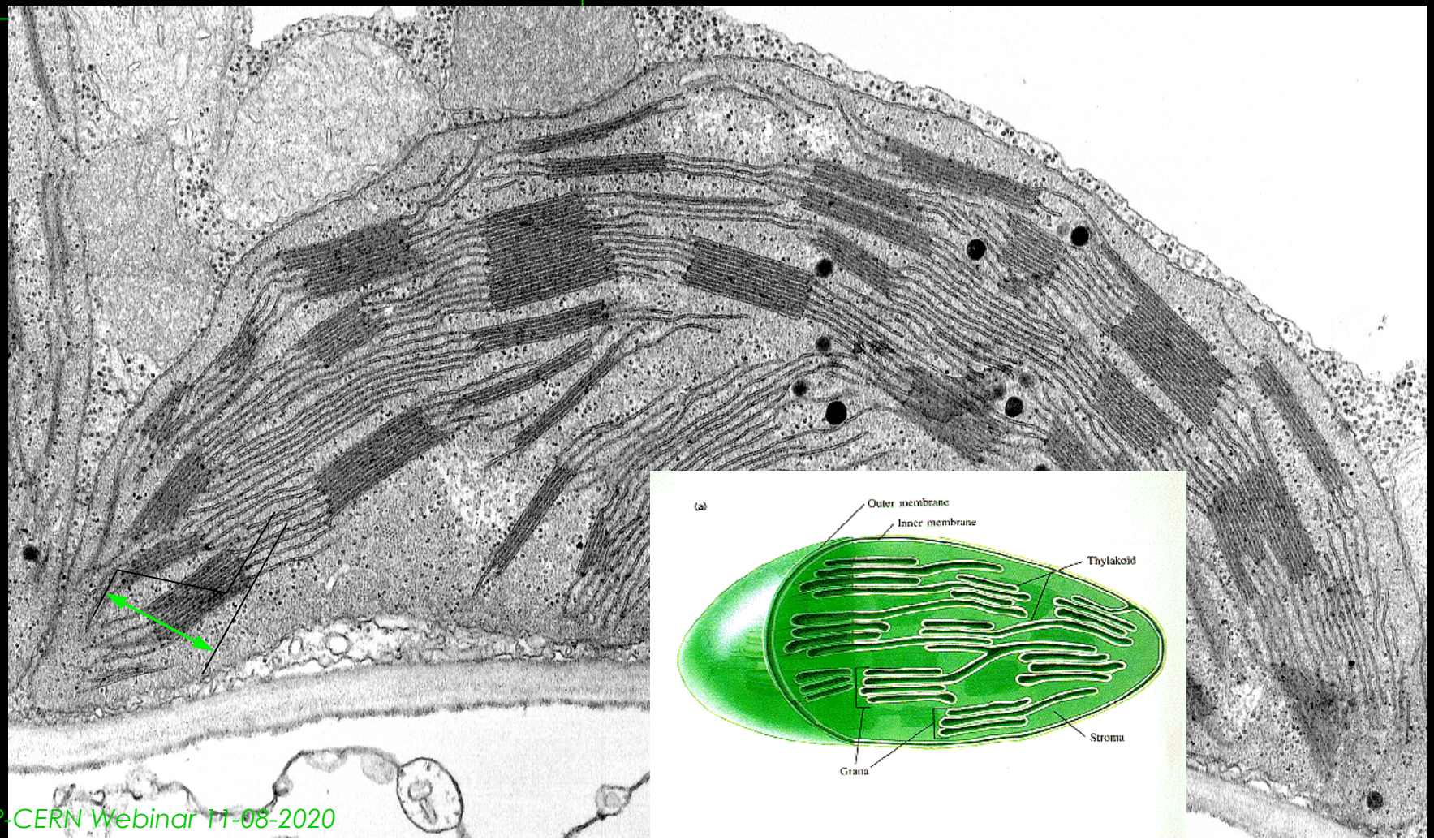


<10nm

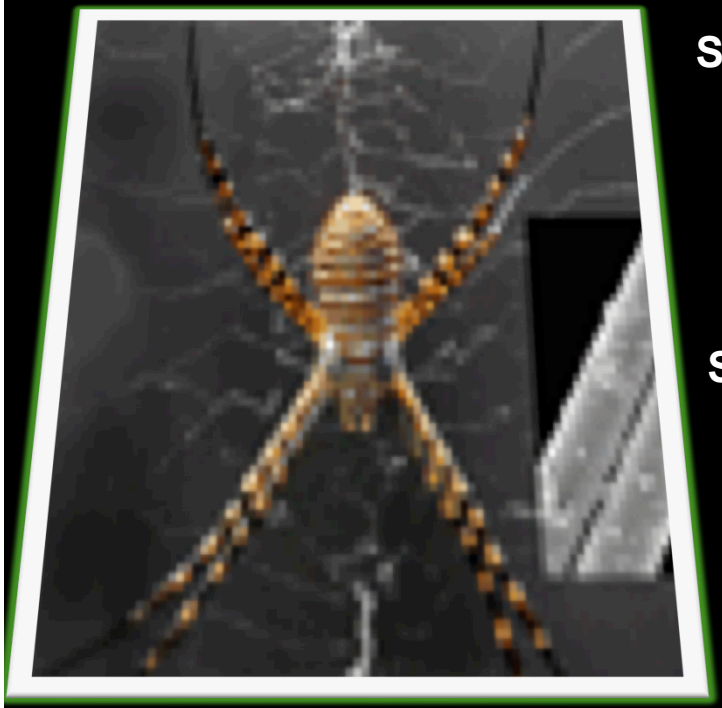
NANO IN NATURE: NAT. PHOTOSYNTHESIS

Photon Absorption — Photo Chemistry — e-Transport — Biochemistry — Physiology

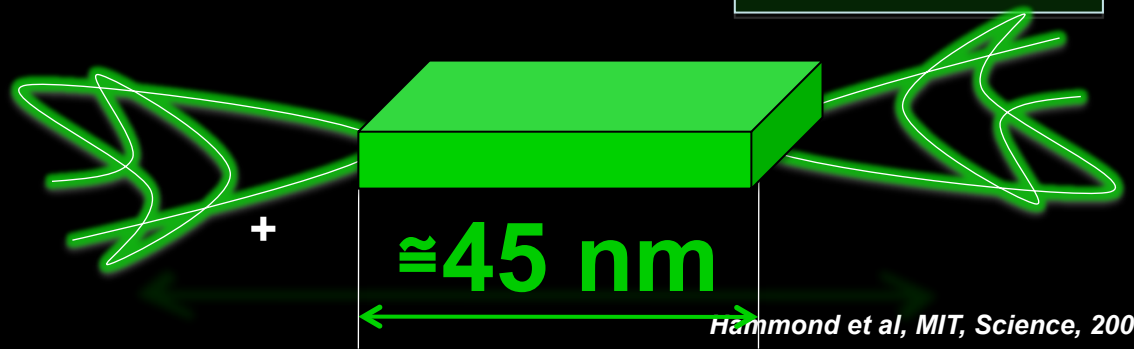
fs — ps — ns — ms — ms-s — >>> 1s



U2ACN2: NANO IN NATURE



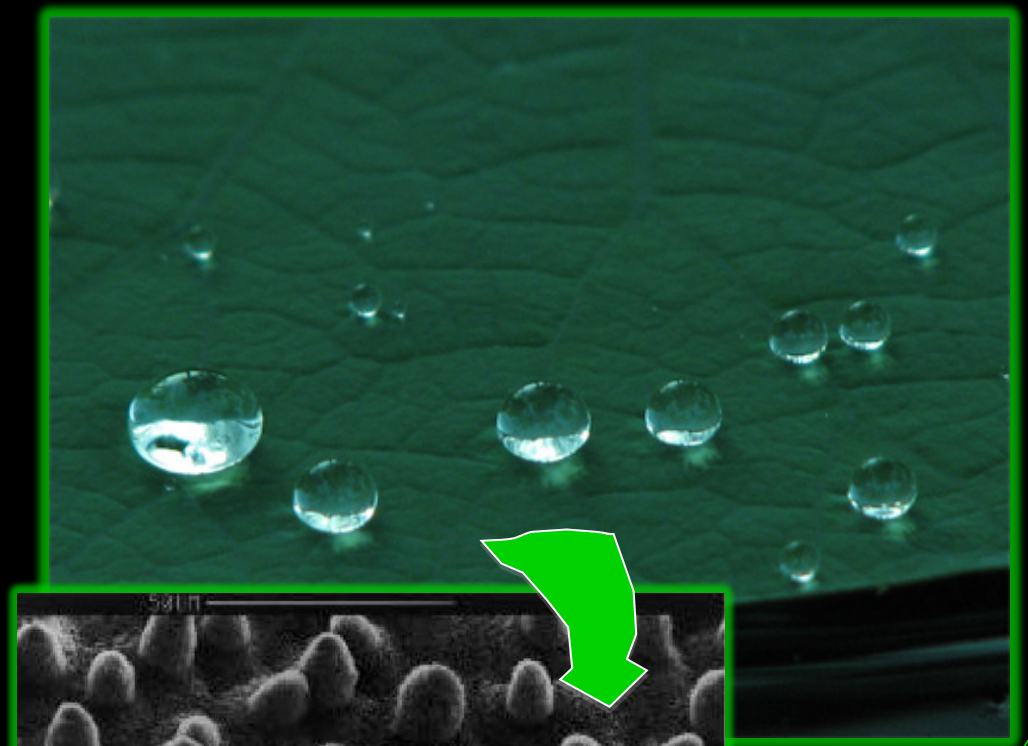
	Density (g/cm^3)	Elasticity Modulus (GPa)	Tensile strength (GPa)	Breaking Strain (%)	Toughness (MJ/m^3)
Spider Silk					
Argiope trifasciata	1.3	1-10	1.2	30	100
Nephila clavipes	1.3	1-10	1.8	30	130
Silkworm					
Bombyx mori	1.3	5	0.6	12	50
Nylon 6.6	1.1	5	0.9	18	80
Kevlar 49	1.4	130	3.6	3	50
PBO	1.6	270	5.8	3	70
Steel	7.8	200	3.0	2	6

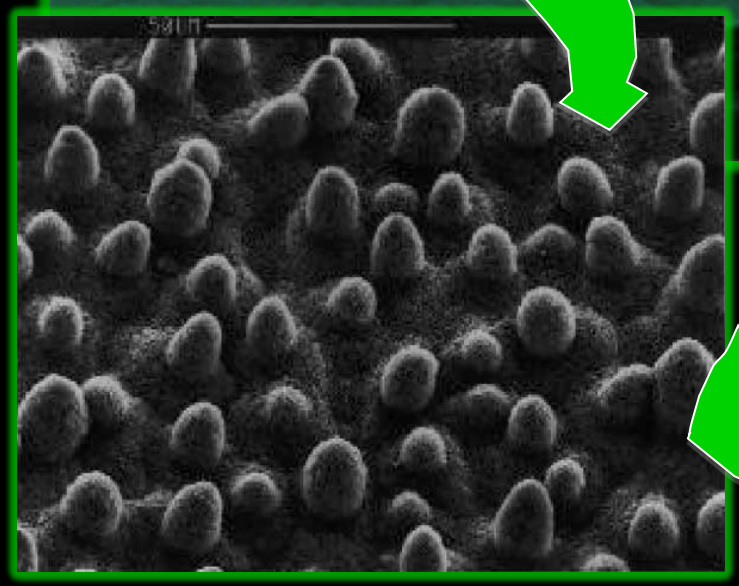


S.P.-2015, Pakistan 26-29/08/2015

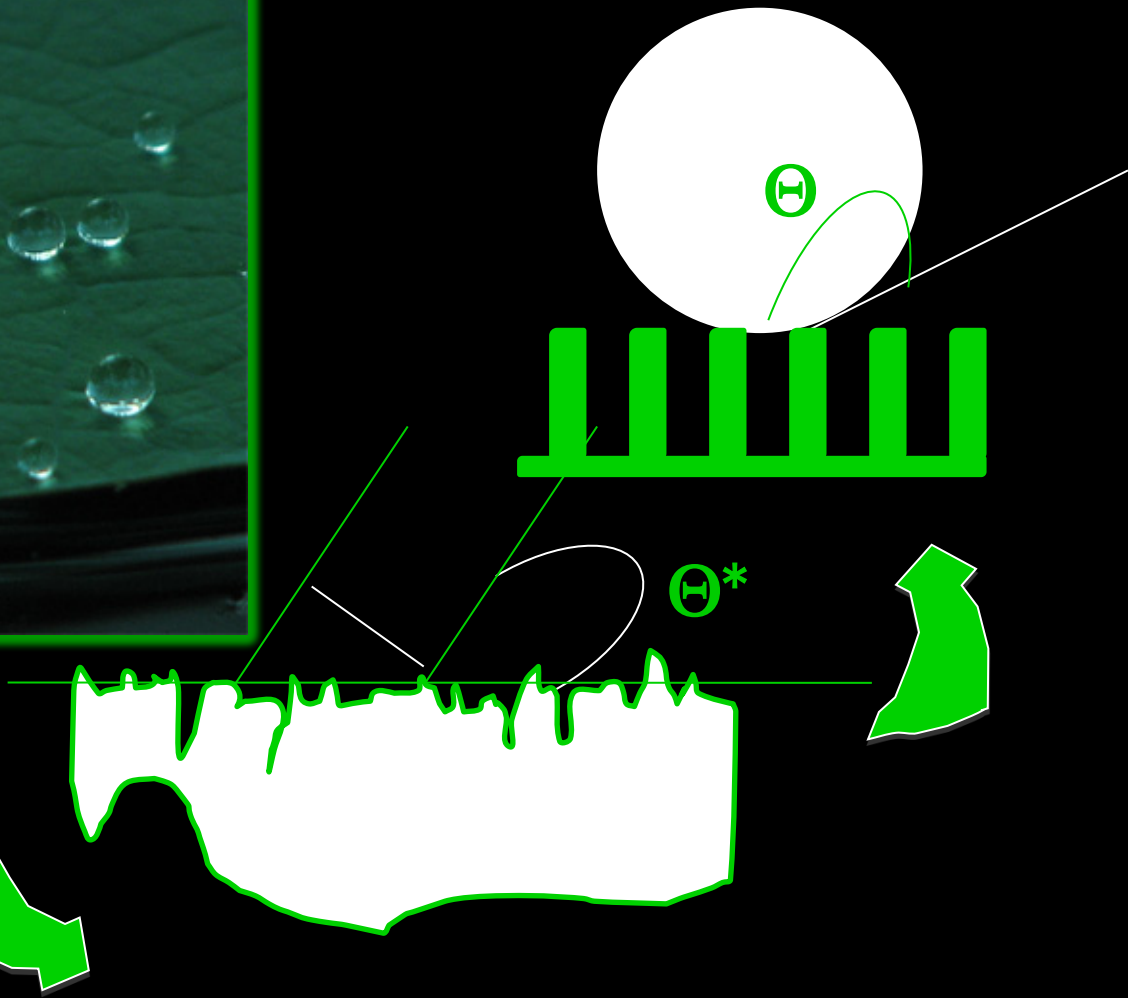
Hammond et al, MIT, Science, 2005

NANO IN NATURE: LEAVE' SURF. TENSION





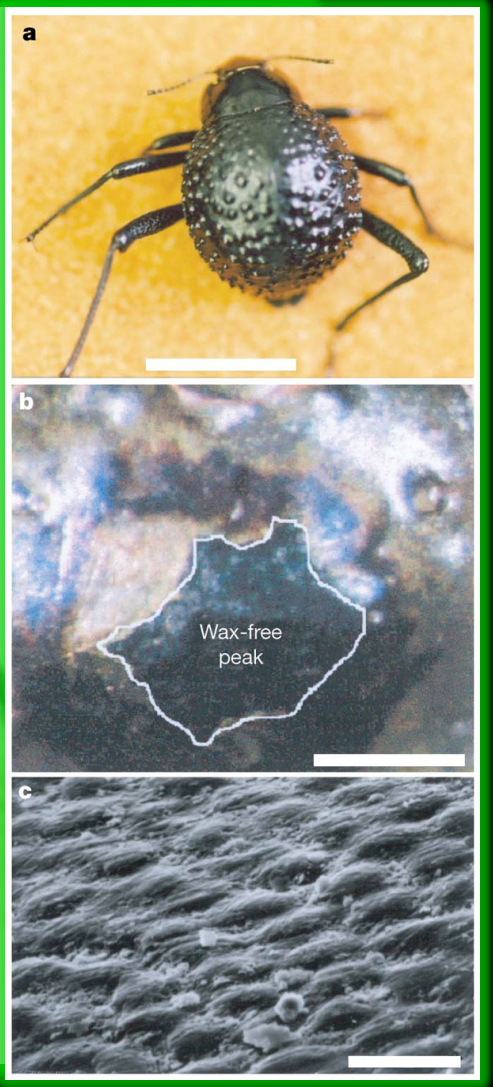
40 nm



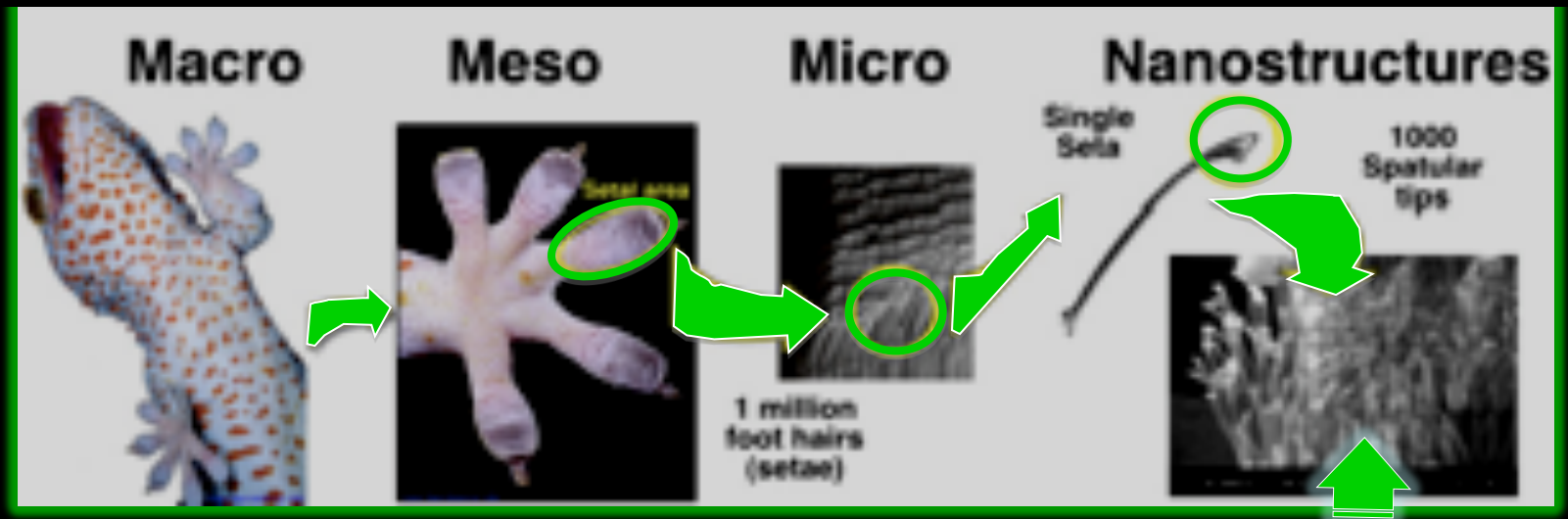
$$\cos\Theta^* = f_1 \cos\Theta_1 + f_1 \cos\Theta_2)$$

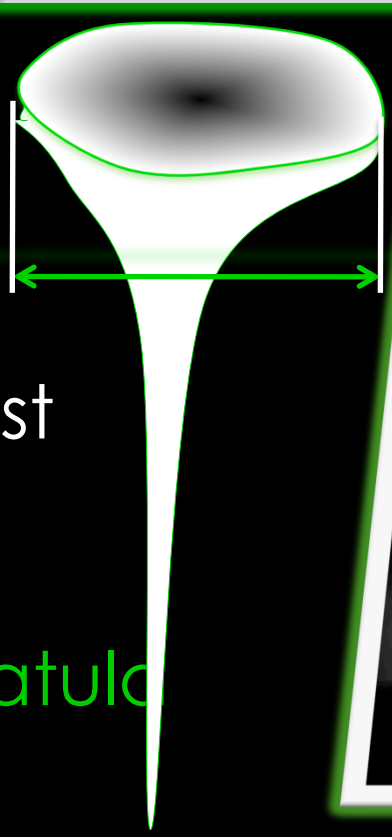
Barthlott, W., Neinhuis, C. Planta 1997, 202, 1-8.

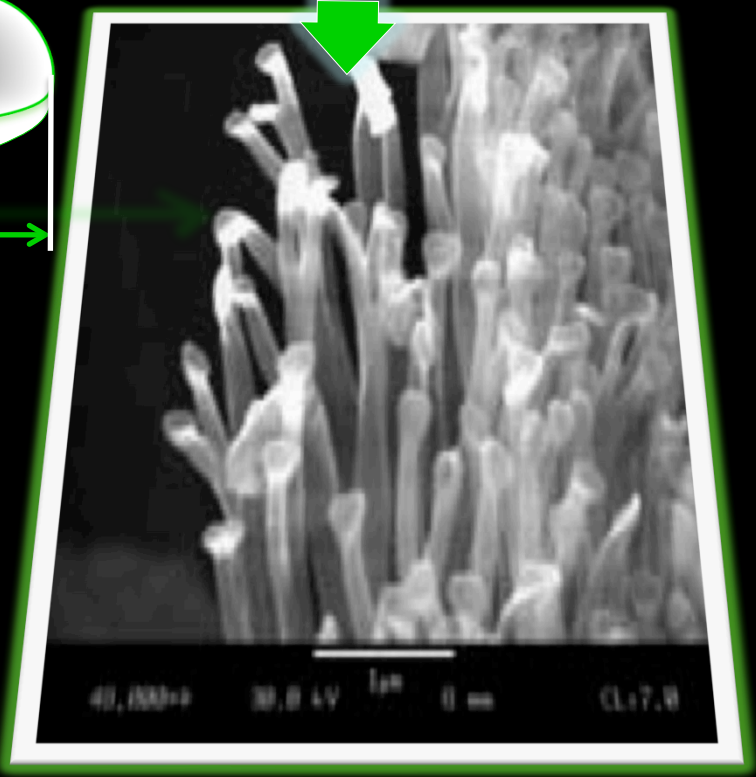
NANO APPLICATIONS:
SURFACE TENSION TUNABILITY



NANO IN NATURE: GECKO ADHESIVE SYST.







≅250 nm

-Gecko's adhesion syst
& Van der Waals.
-m-elastic hairs: Setae
Setae: nano-fibers Spatula

Acknowledgments

- UNESCO & IAEA.
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- African Laser Centre, Pretoria-South Africa.
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- Organization of Women in Science for the Developing World, Trieste-Italy.
- International Centre for Science & Technology-UNIDO, Trieste-Italy.
- Centre National pour la Recherche Scientifique, Paris-France.
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