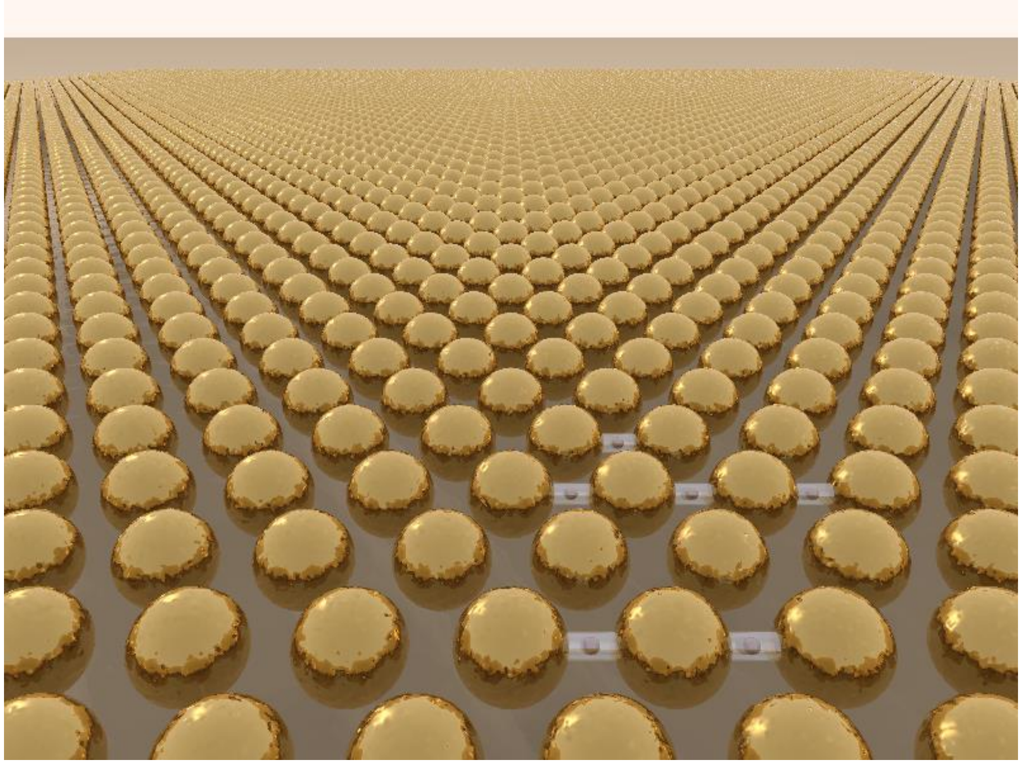

Electron transport : From nanoparticle arrays to single nanoparticles

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Hongyue Wang (PhD)
Helena Moreira (PhD)
Limin Cui (Visitor)
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LPEM - ESPCI

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QTG

LPEM
Laboratoire de Physique et d'Etude des Matériaux

ESPCI ParisTech

cnrs

AGENCE NATIONALE DE LA RECHERCHE ANR

SUMMARY

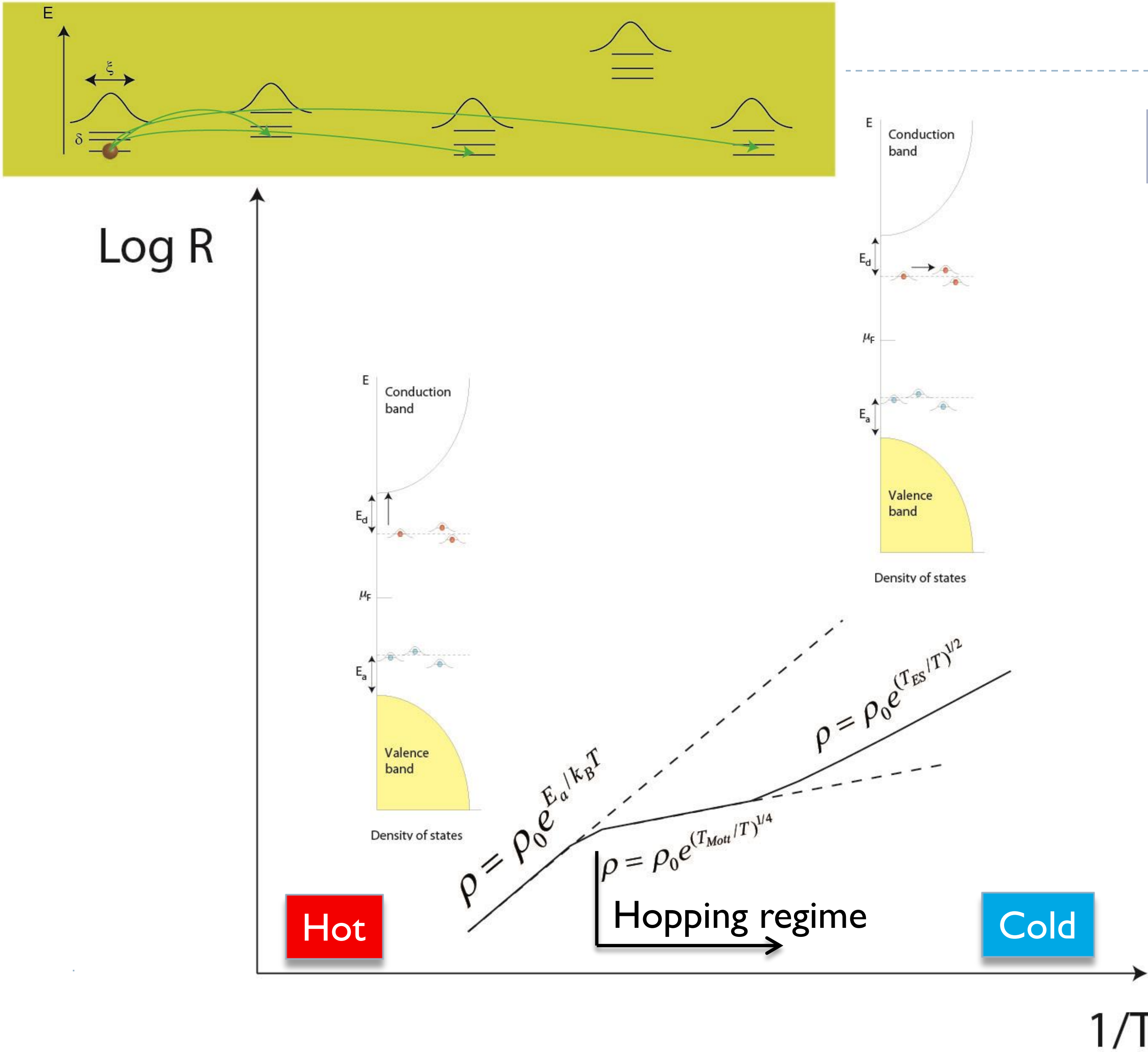
Part I – Transport in nanoparticle arrays

- Electron transport in disordered systems
  - Doped semiconductors against granular metals
- Co-tunneling transport in gold nanoparticles arrays
  - Efros-Shklovskii and Middleton-Wingreen

Part II – Transport in single nanoparticle devices

- In-Vacuum projection of nanoparticles for on-chip tunneling spectroscopy
- Verwey transition in single magnetite nanoparticles

Variable Range Hopping in semiconductors



VRH Laws

$$\sigma = \sigma_0 \exp-(T_0 / T)^{\alpha}$$

Mott Law

Mean Level Spacing

$$T_{Mott} \propto \delta \propto \frac{1}{\xi^3}$$

$$\alpha = 1/4$$

Efros-Shklovskii Law

Coulomb Energy

$$T_{ES} \propto \frac{e^2}{\xi}$$

$$\alpha = 1/2$$

Efros-Shklovskii law in bulk semiconduting CdSe

Zhang, Y. et al. Probing the Coulomb Gap in Insulating n-Type CdSe.
Physical Review Letters **1990**, *64*, 2687–2690.

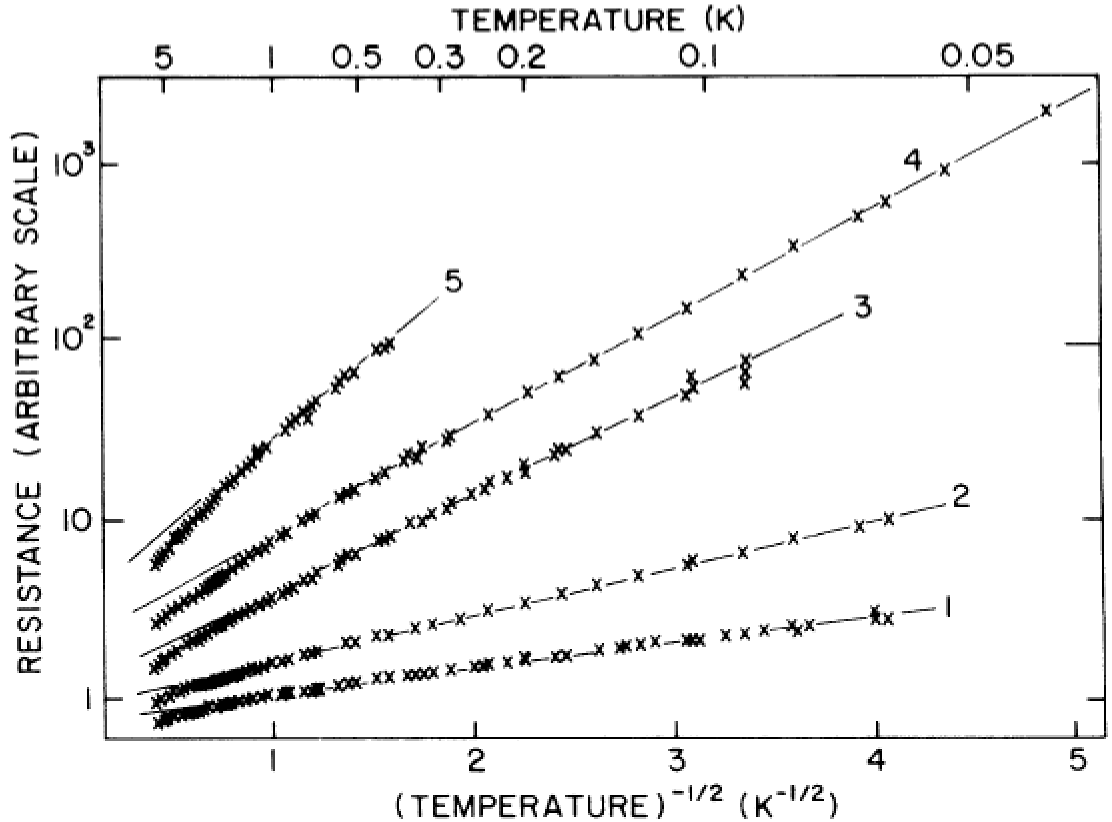
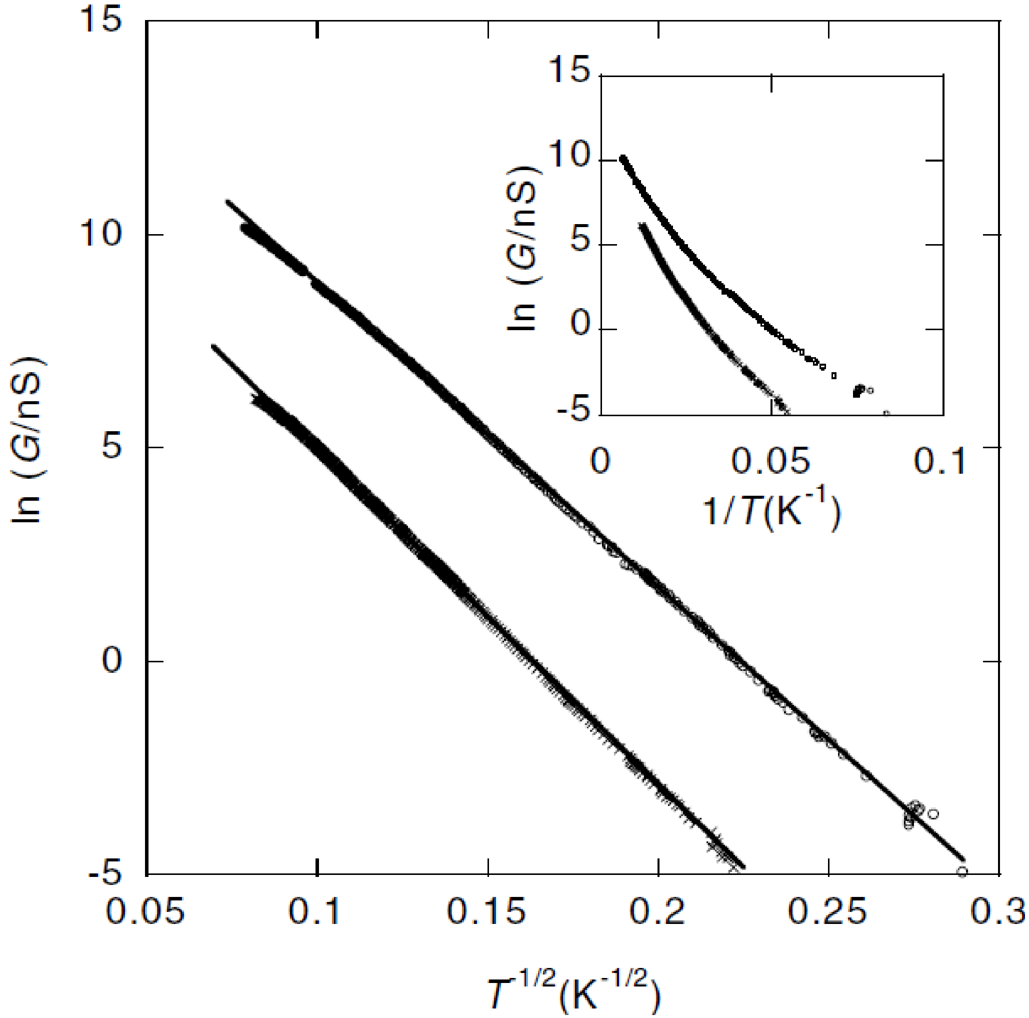
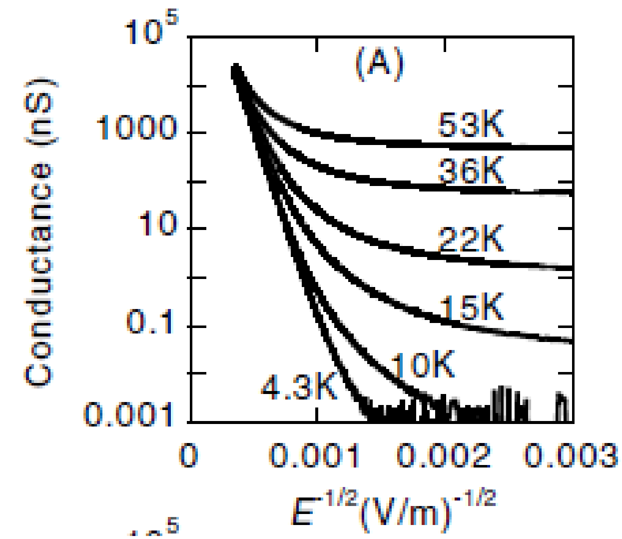


FIG. 2. Resistance of five insulating *n*-type CdSe samples plotted as a function of $T^{-1/2}$ on a semilogarithmic scale.

Efros-Shklovskii law in semiconduting CdSe nanoparticles films

Yu, D.et al. Variable Range Hopping Conduction in Semiconductor Nanocrystal Solids. *Physical Review Letters* 2004, 92, 216802.





Evaporated metal thin films

Platinum film between 0.1 nm and 10 nm thick

I.Neugebauer et al. *JAP* **33**, 74 (1962).

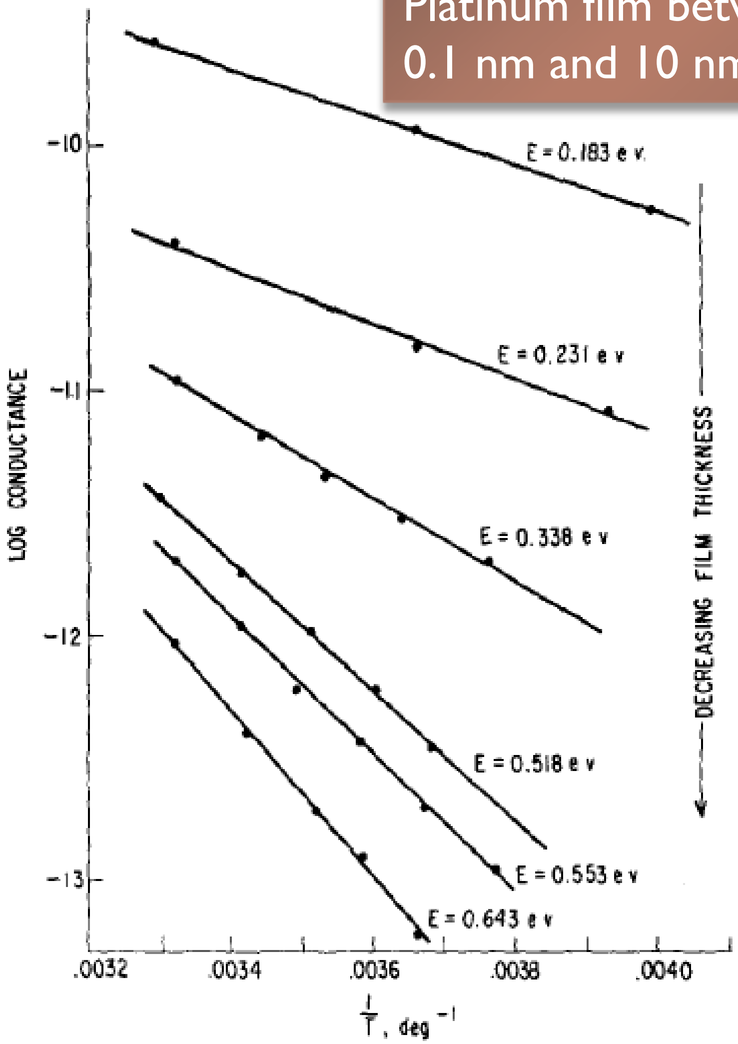
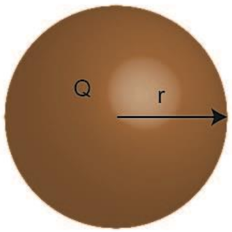


FIG. 8. Log conductance vs reciprocal temperature for platinum films of different thicknesses.

Coulomb energy

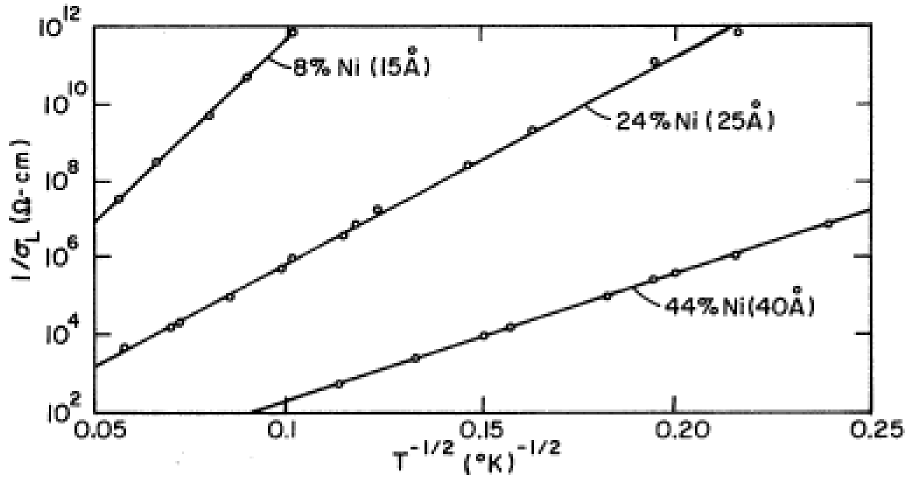


$$\phi(r) = \frac{Q}{4\pi\varepsilon\varepsilon_0 r}$$

$$C_{self} = Q = 4\pi\varepsilon\varepsilon_0 r$$

$$E_C = \frac{e\phi}{2} = \frac{e^2}{2\times 4\pi\varepsilon\varepsilon_0 r} = \frac{e^2}{2C_{self}}$$

Efros-Shklovskii law in disordered metal thin films !!!



1.Sheng, P., Abeles, Ni films
Physical Review Letters **31**, 44-47 (1973).

$$\sigma = \sigma_0 \exp(-(T_0 / T)^{1/2})$$

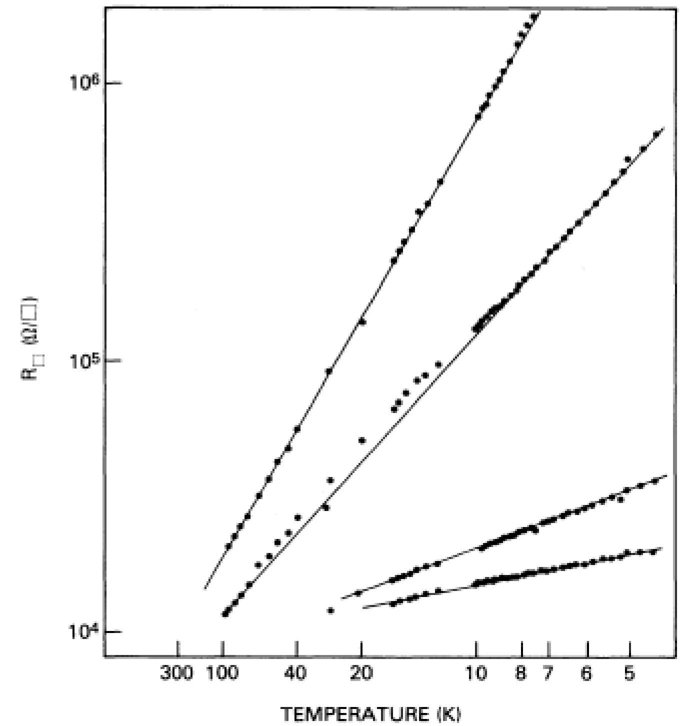
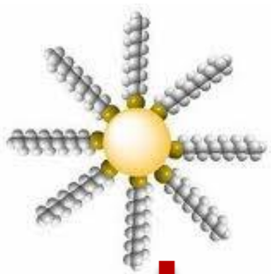


FIG. 4. The logarithm of the sheet resistance as a function of $1/\sqrt{T}$ for a variety of the nonsuperconducting samples. The lines are guides to the eye.

Simon, R. et al. granular niobium nitride cermet films
Physical Review B **36**, 1962-1968 (1987).

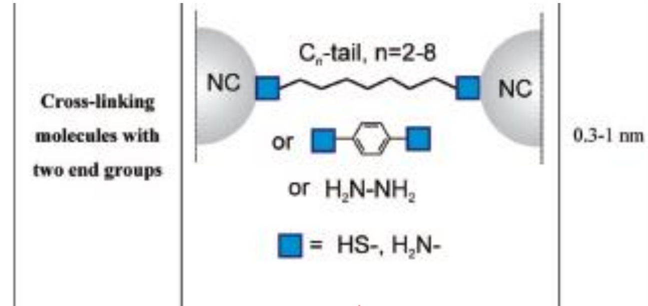
Electron transport in metallic nanocrystals arrays - sample preparation

Synthesis
- Brust method(1992)
- Revisited by Klabunde (1998)

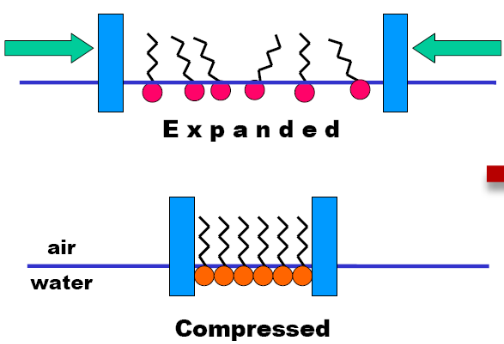


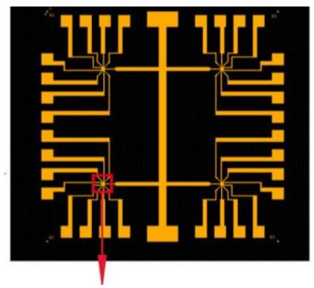
∅ ~ 5nm

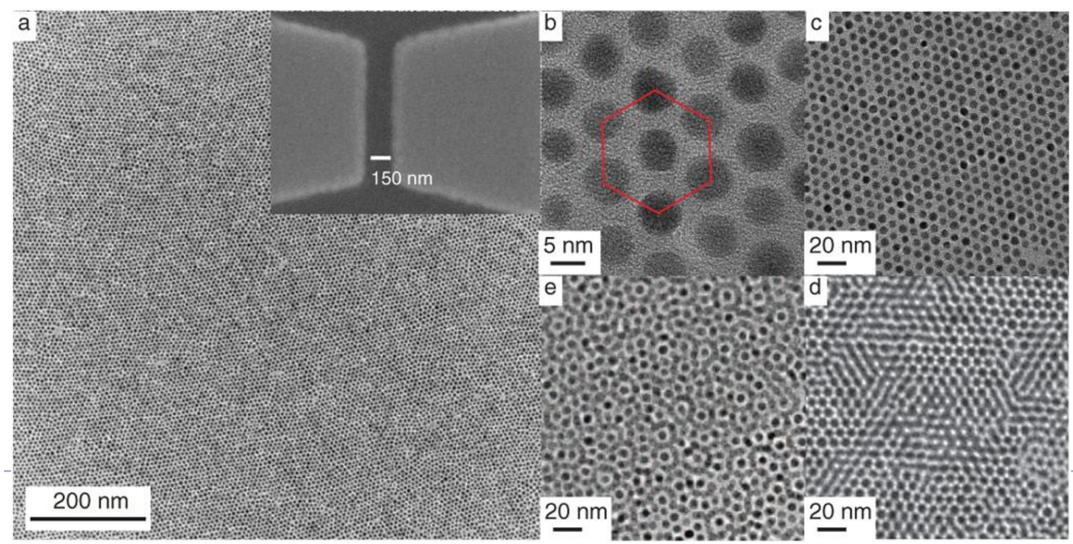
Arrays crosslinked by alcane dithiol molecules



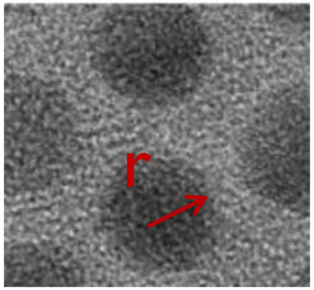
Arrays formed by the Langmuir method



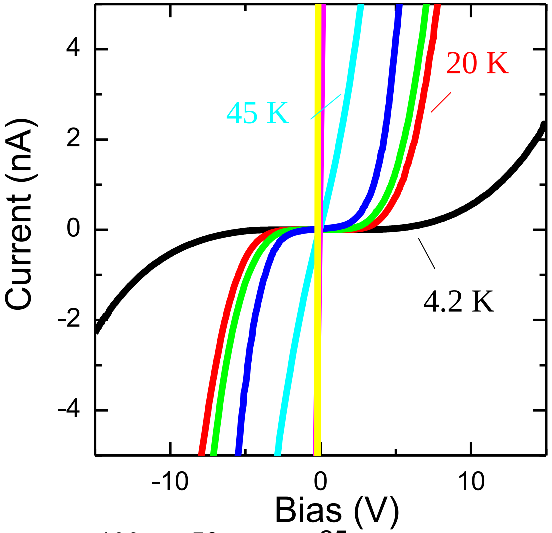




Electron transport in nanocrystals arrays (as function of temperature)



$$C_{self} = Q = 4\pi\varepsilon\varepsilon_0 r$$

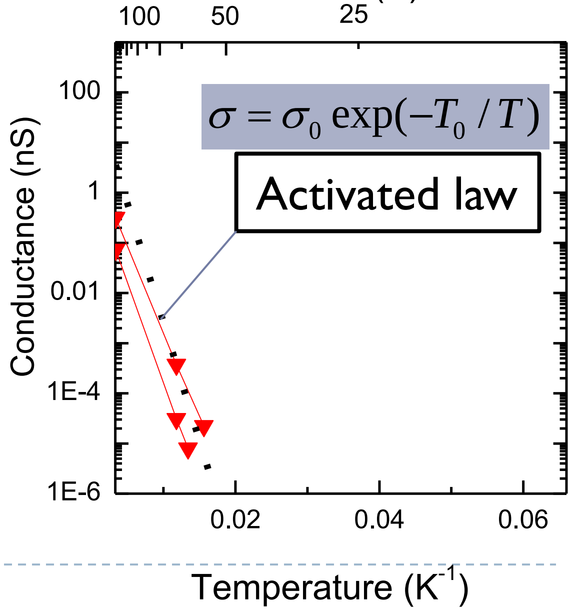


Coulomb energy

$$E_C = \frac{e^2}{2C_{self}} = k_B T_0 = e^2 / 4\pi\varepsilon\varepsilon_0 r$$

$$\approx 1100K$$

$$(r \approx 2.5nm, \varepsilon \approx 3)$$



Efros-Shklovskii law in nanocrystals arrays (as function of temperature)

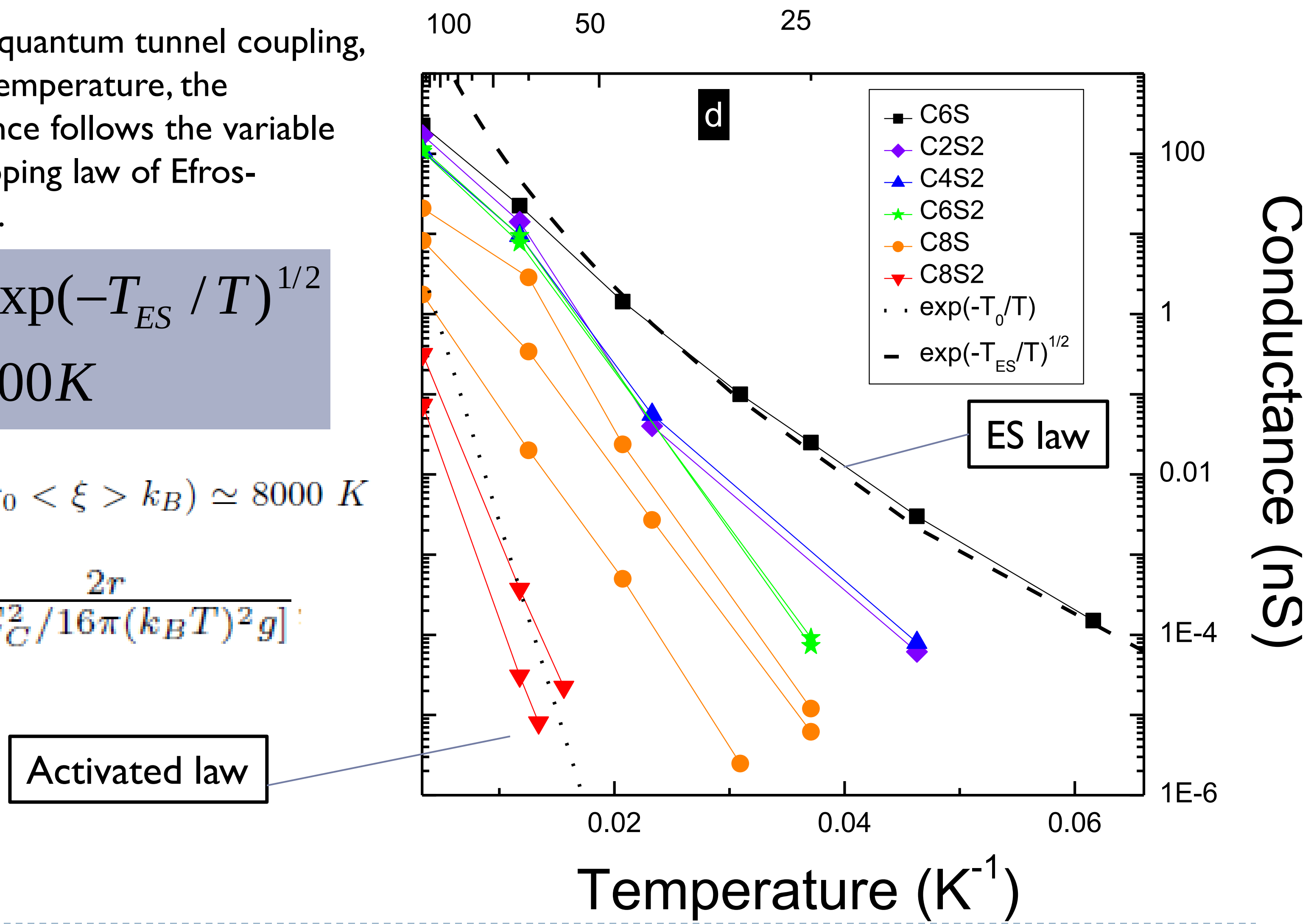
- At larger quantum tunnel coupling, and low temperature, the conductance follows the variable range hopping law of Efros-Shklovskii.

$$\sigma = \sigma_0 \exp(-T_{ES} / T)^{1/2}$$

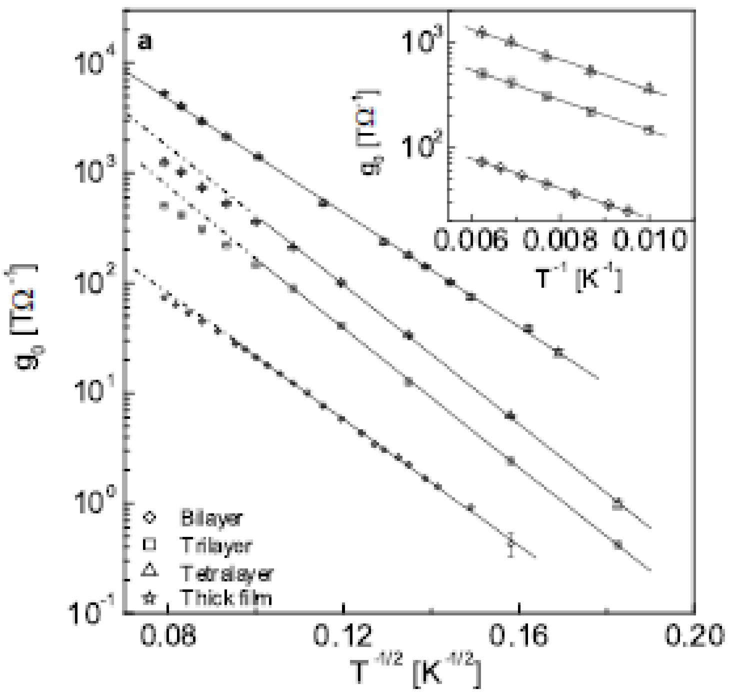
$$T_{ES} \approx 8000K$$

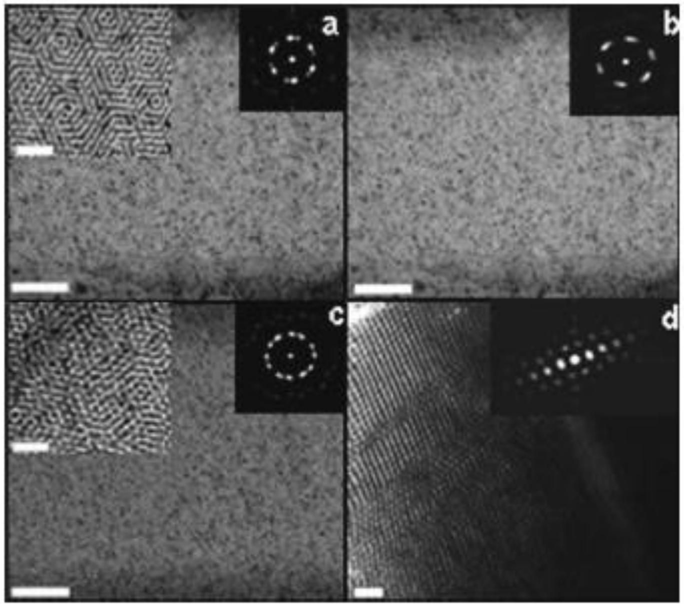
$$T_{ES} = e^2/(4\pi\varepsilon\varepsilon_0 < \xi > k_B) \simeq 8000\ K$$

$$\xi = \frac{2r}{\ln\left[E_C^2/16\pi(k_B T)^2 g\right]}$$



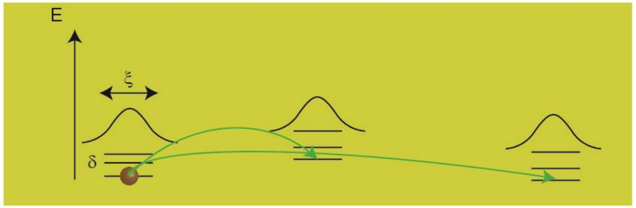
Efros-Shklovskii law in nanocrystals array H. Jaeger's group (Chicago)



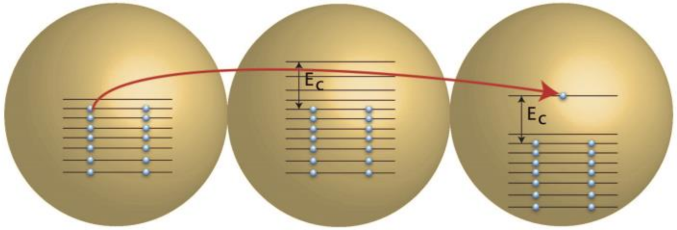


1. Tran, T.B. *et al. Physical Review Letters* **95**, 076806 (2005).

Why is Efros-Shklovskii law in granular metallic systems surprising ?

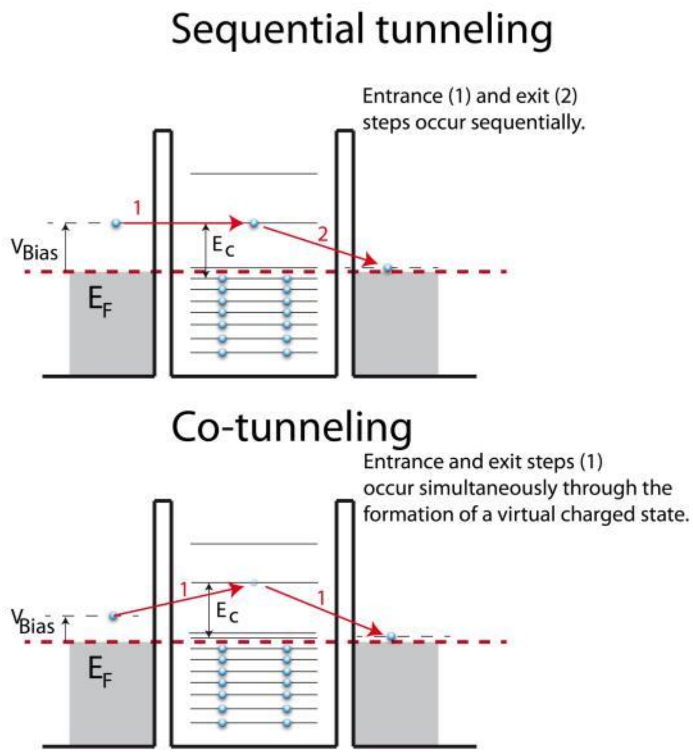


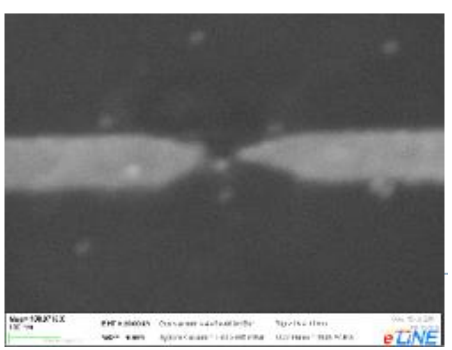
- In semiconductors, direct long distance tunneling is possible



- Long distance tunneling between metallic grains is not possible

« co-tunneling »

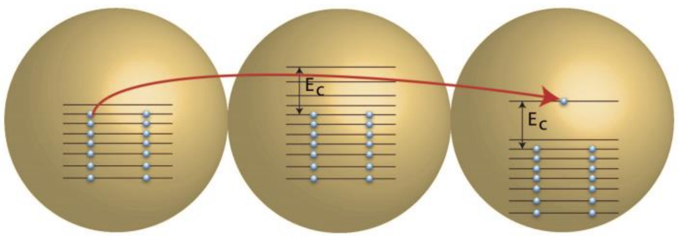




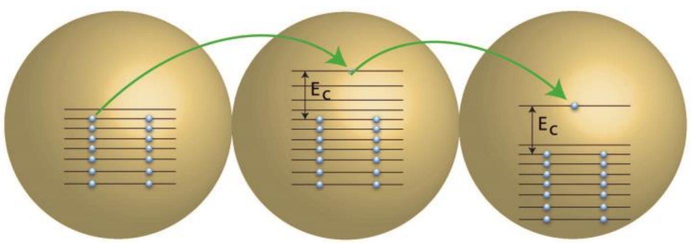
- At low temperature, electron transport is blocked because of the large Coulomb energy $E_c=e^2/2C$

- As tunnel coupling between the nanocrystal and the electrodes becomes large, electron tunneling through virtual charged states become possible. <u>This is cotunneling.</u>

Efros-Shklovskii law in granular metals explained by « co-tunneling »



- Single long distance tunneling is not possible



- Simultaneous multiple short distance tunneling events is possible

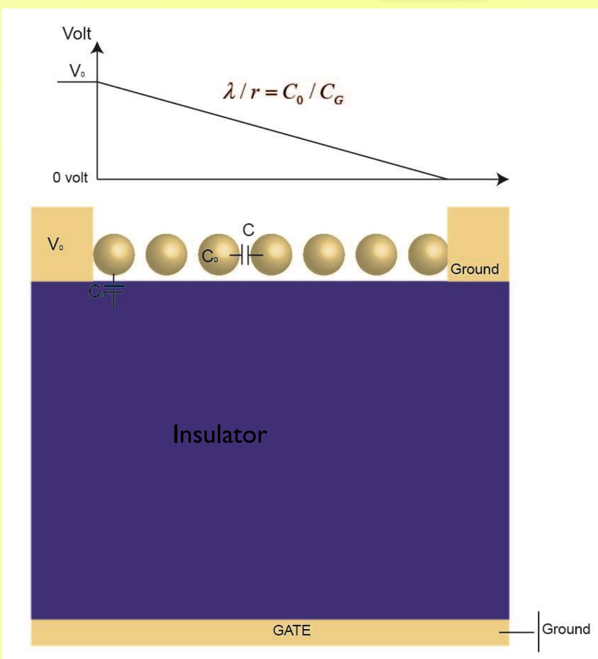
- *[1]* Jingshan Zhang and Boris I. Shklovskii, Physical Review B **70**, 115317 (2004)
- *[2]* M.V. Feigel'man and A.S. Ioselevich, Jetp Letters **81**, 277 (2005)
- *[3]* I. Beloborodov, A. Lopatin, and V. Vinokur, Physical Review B **72**, 125121 (2005).
- *[4]* I. S. Beloborodov, A. V. Lopatin, V. M. Vinokur, and K. B. Efetov, Reviews of Modern Physics **79**, 469-518 (2007).

Electron transport in nanocrystals arrays (as function of electric field)

Long Screening length

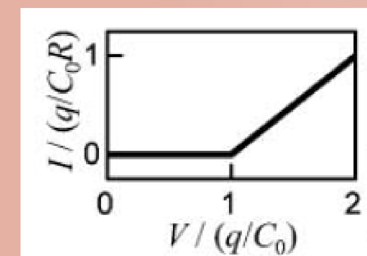
$$I = I_0 \exp(-(E_{Coulomb} / k_B T)^{\alpha})$$

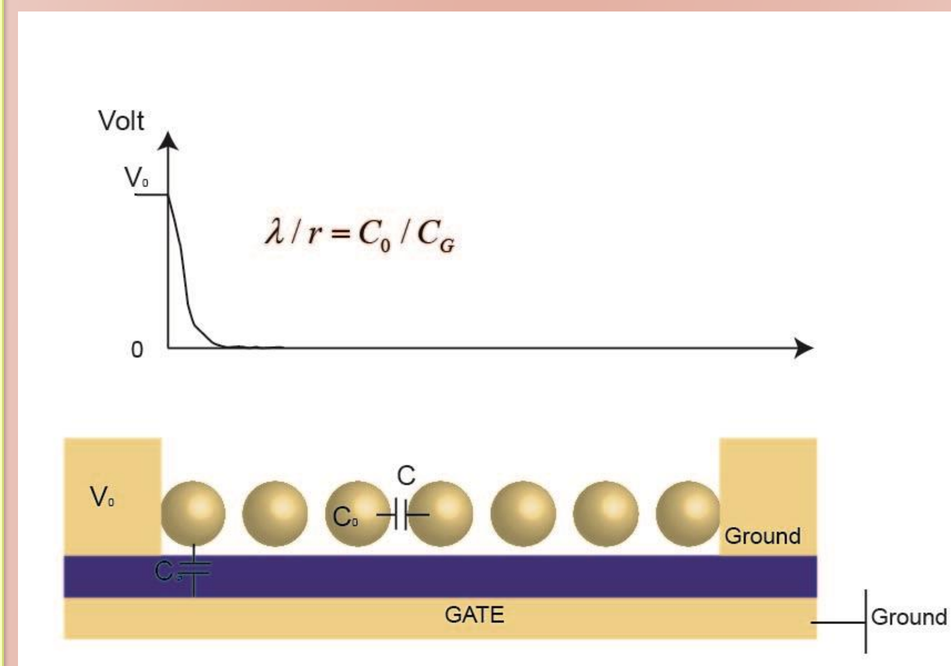
$$I = I_0 \exp(-(E_{Coulomb} / eV)^{\alpha})$$



Short Screening length
→Middleton-Wingreen

$$I \propto (V - V_T)^{\alpha}$$



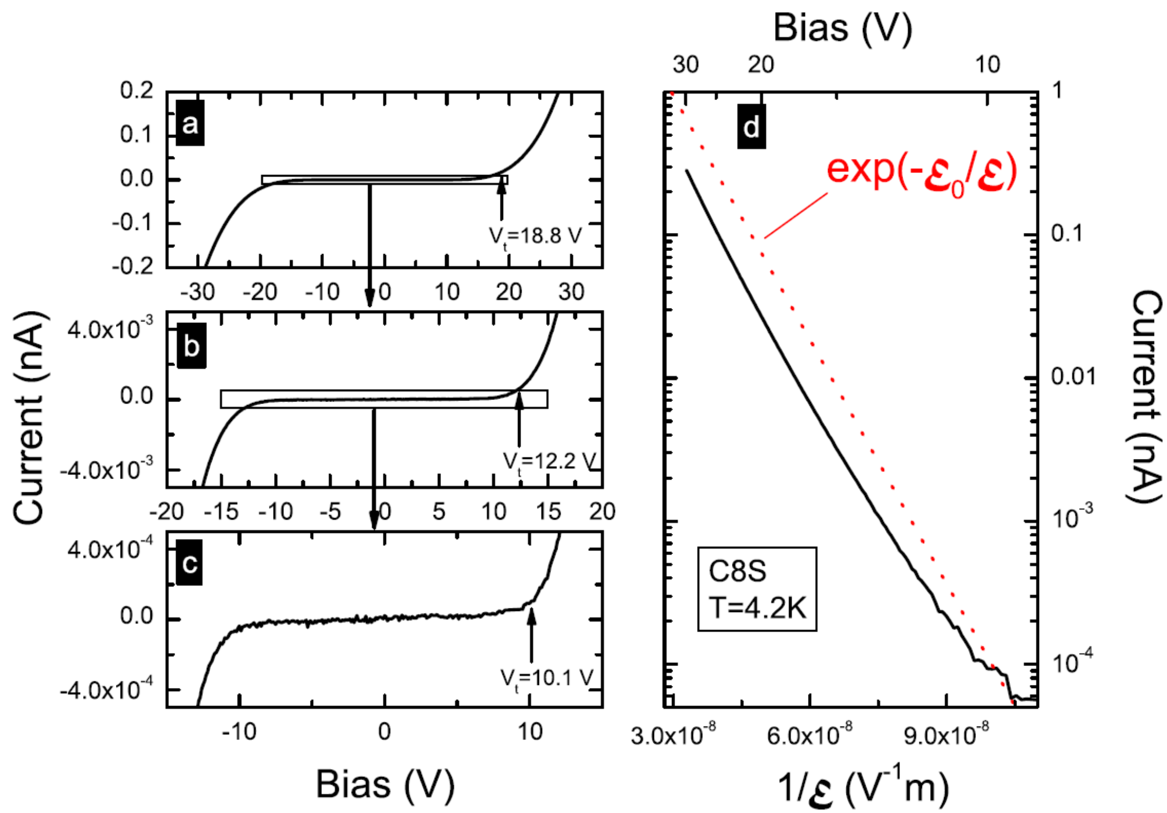


In our arrays, Long Screening length model applies

- Weak capacitive coupling with the gate

- Short distance between electrodes ~150 nm

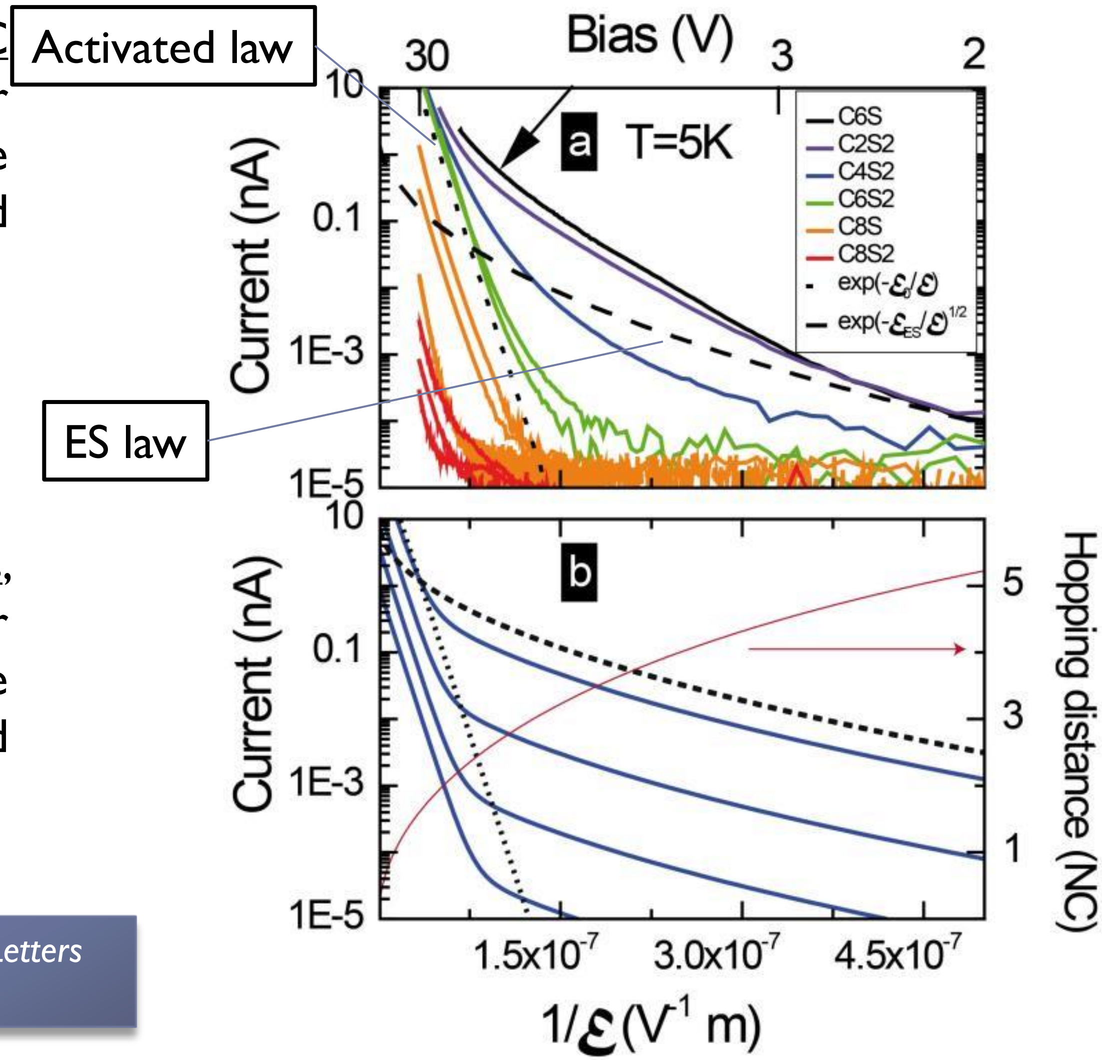
- Threshold voltage is not relevant



Electron transport in nanocrystals arrays (as function of electric field)

- <u>For weakly conducting NC arrays</u>, i.e. small tunnel barrier transparency, the I(V) curve follows an activated law, dotted line.

- <u>For better conducting arrays</u>, i.e. for larger tunnel barrier transparency, the I(V) curve follows an ES-type law, dashed line

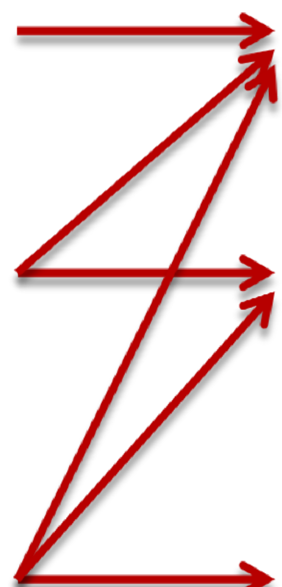


H. Moreira *et al. Physical Review Letters* **107**, 176803(2011)

Toward single nanoparticle spectroscopy

Bulk transitions

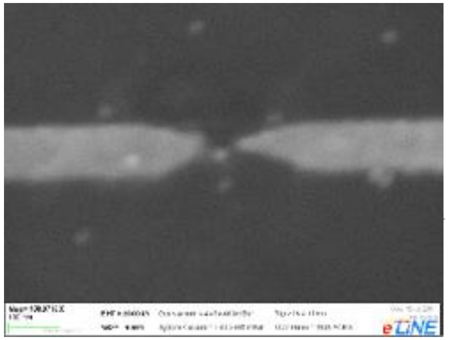
- Anderson Localization
- Mott Localization
- Superconductor-Insulator Transition



Spectral characteristics of single nanoparticles

- Thouless energy
- Coulomb energy
- Superconducting gap

Nanoparticles Trapping



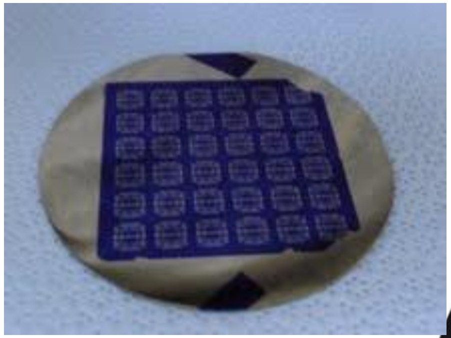
- Goal
  - Trapping a single nanoparticle within the nanogap, (with no parasitic current path)
  - The success rate should be high enough so that the technique can be applied to many different chemically synthesized nanoparticles
  - Can be done in inert atmosphere (argon)

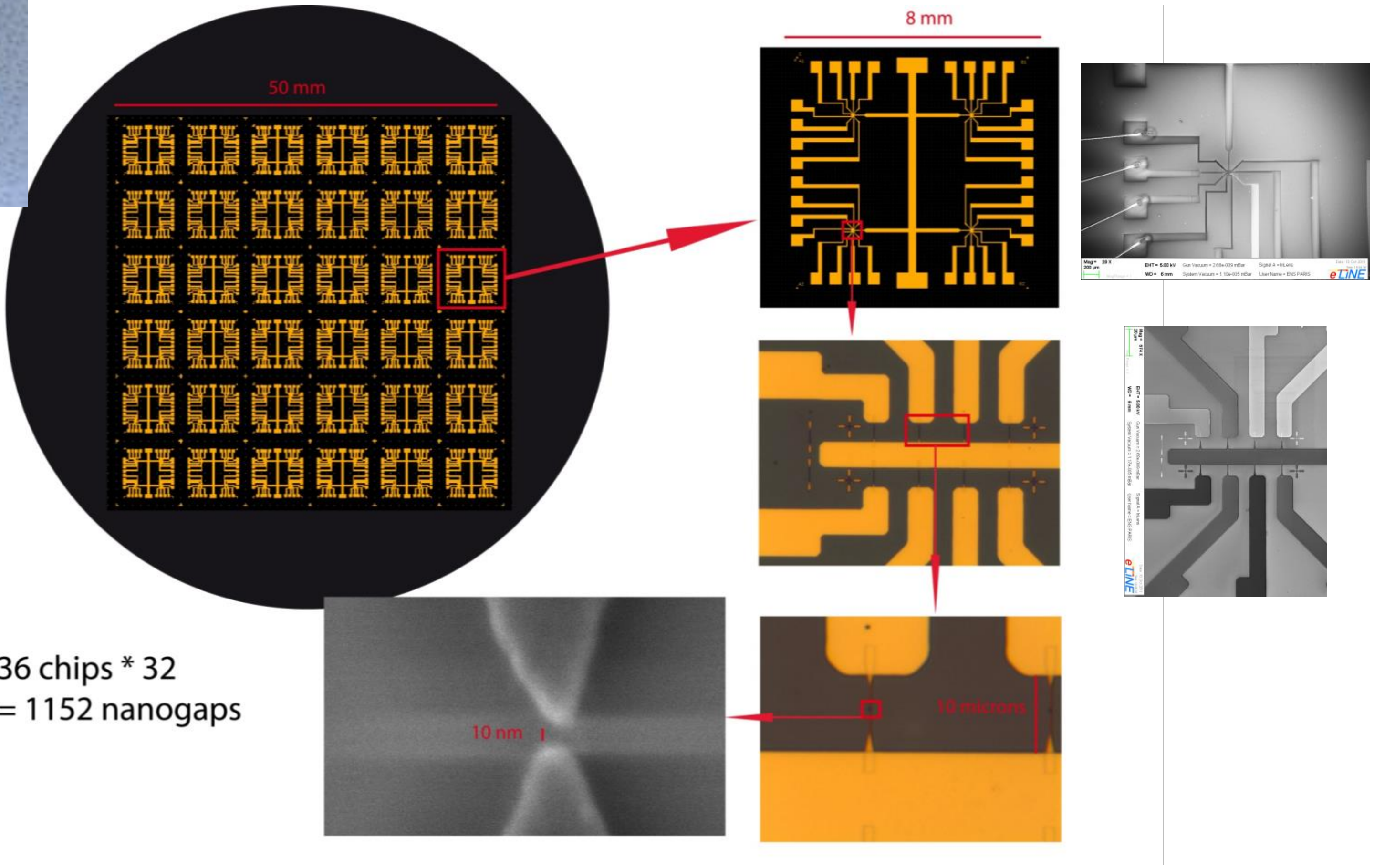
- Method 1 : Electrostatic or molecular assembly in solution
- Method 2 : Method 1+ Dielectrophoretic Force
- Method 3 : nanolithography + one of the other method

→ avoid methods in solution, because of the impossibility of checking tunnel current during assembly

- <u>Method 4 : High vacuum projection of nanoparticles</u>

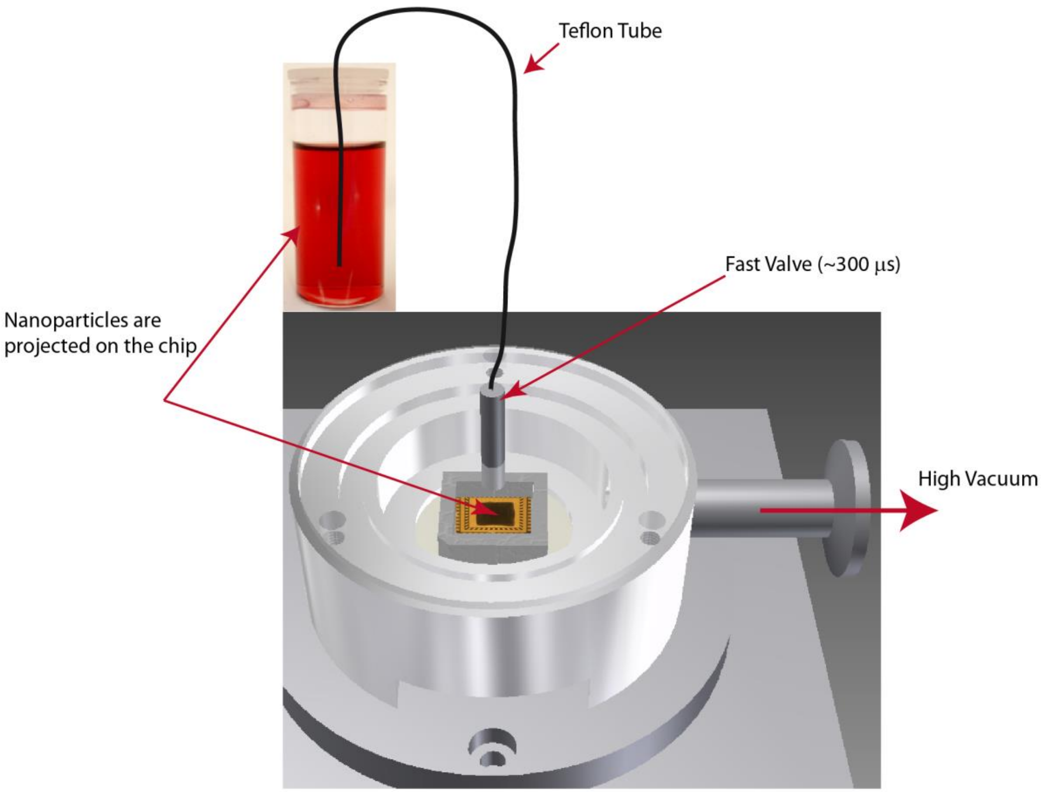
Wafer de nanogaps (LPN – Microfab facility)

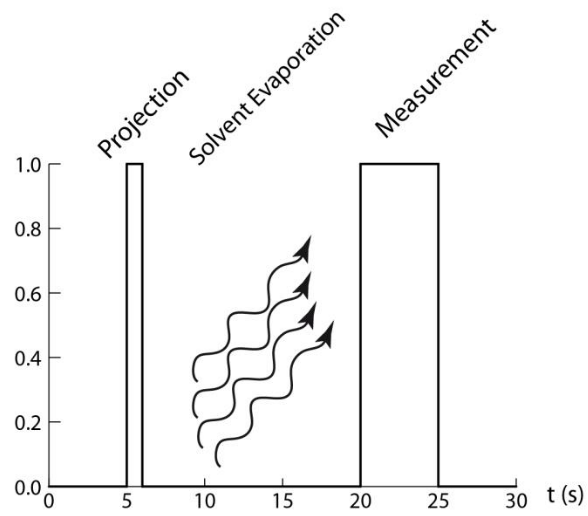




36 chips * 32
= 1152 nanogaps

Method 4: In-vacuum projection of nanoparticles

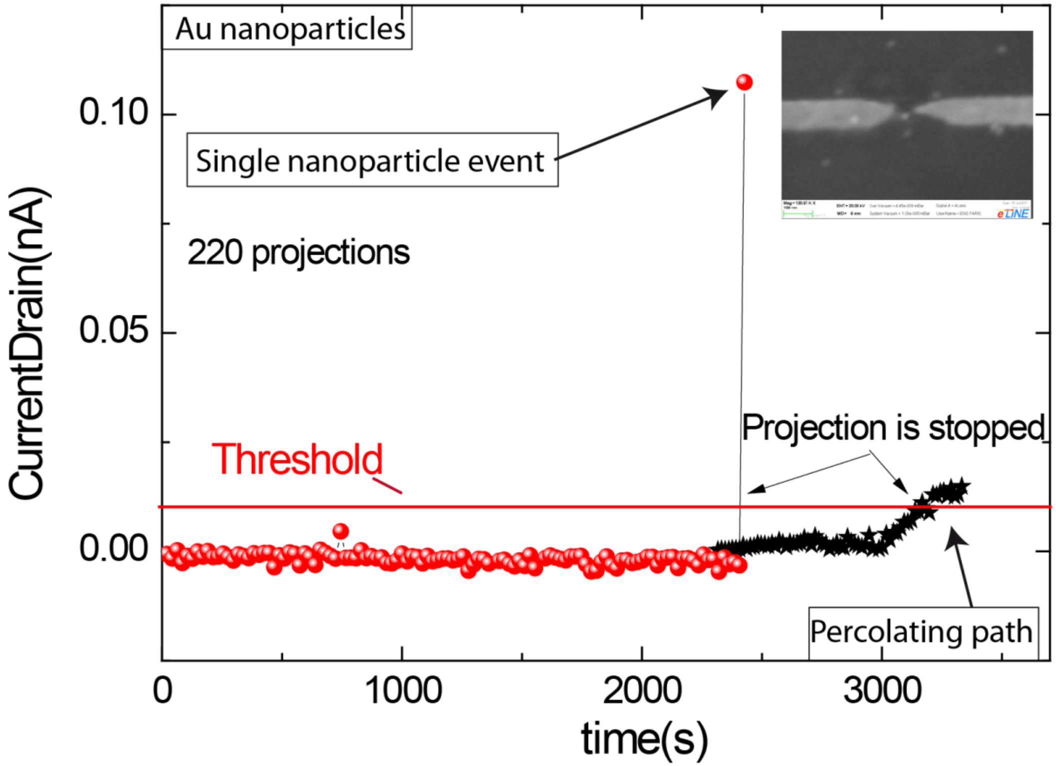




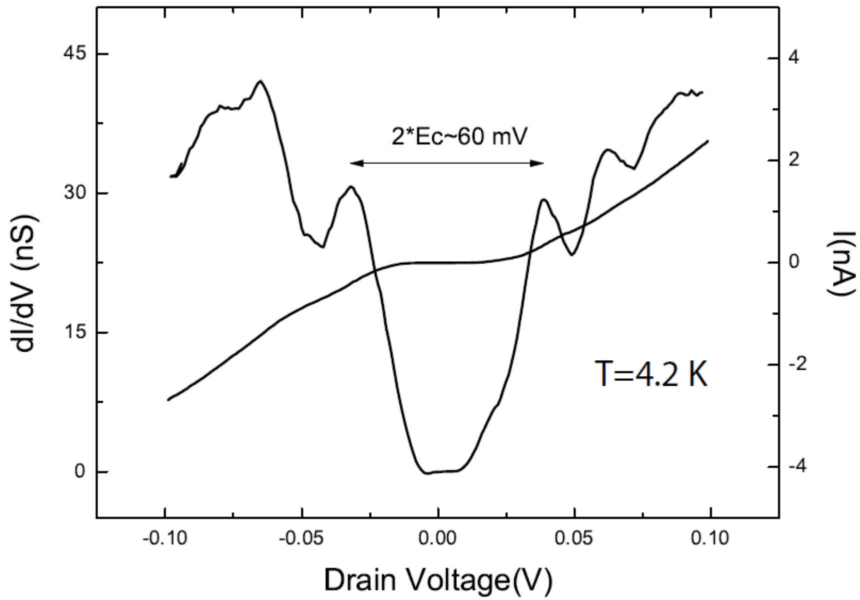
High vacuum chamber used for the projection of nanoparticles on the chip, using a fast pulsed valve(reponse time ~1 ms).

Projection curve

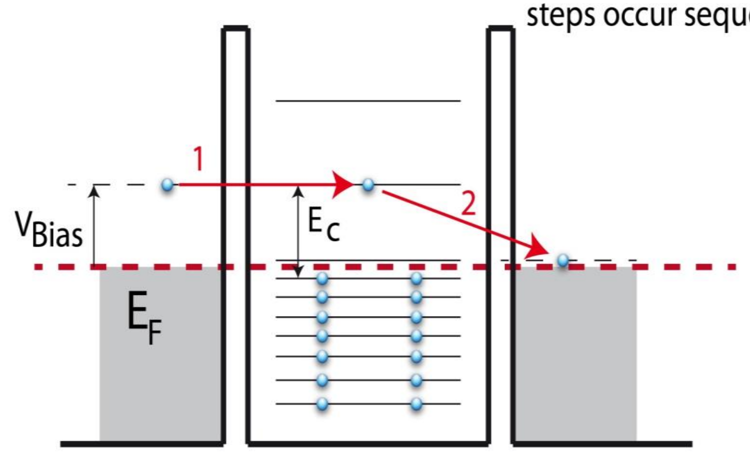
- opening of the valve < 1 ms
- bias voltage = 0.1 V
- Current measured 10s after the projection
- Threshold=0.01nA



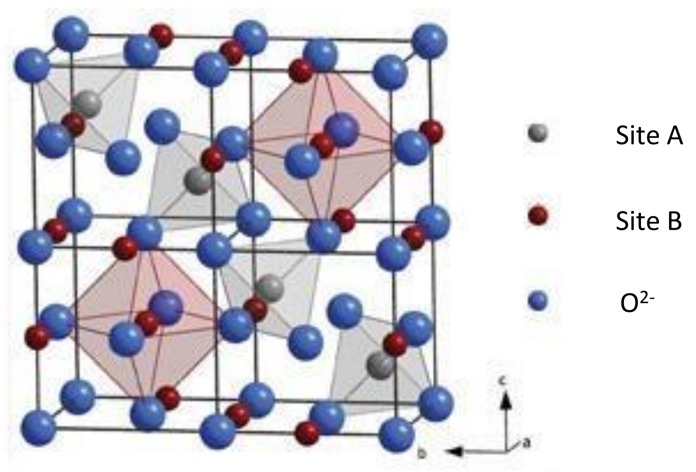
Single gold nanoparticle trapped within the nanogap→ signatures of Coulomb blockade

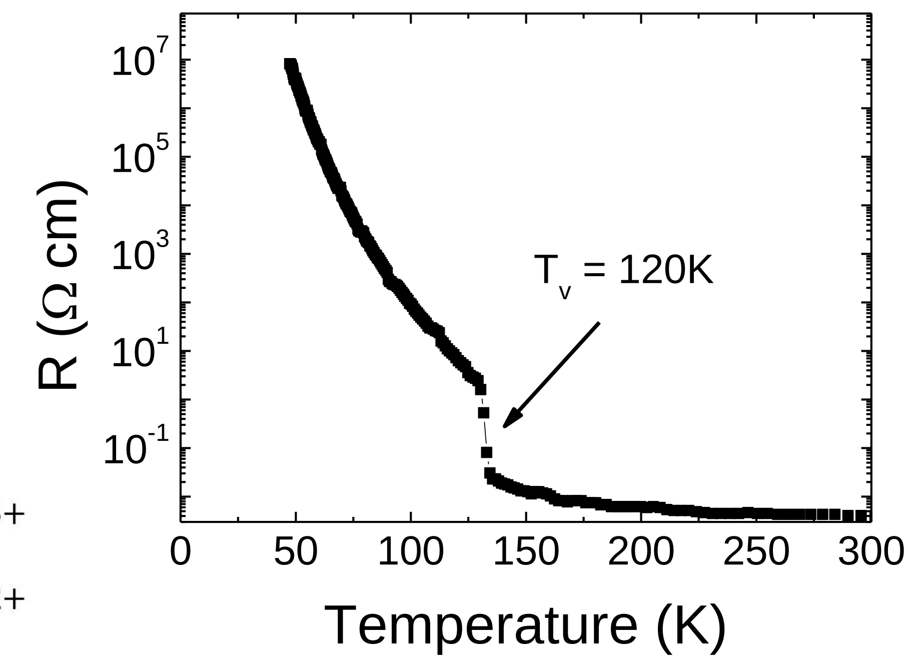


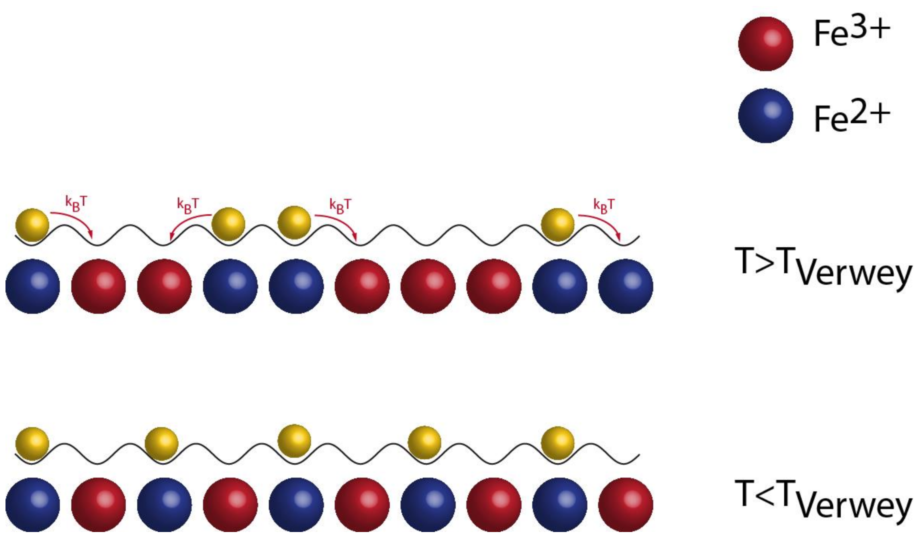
Yu, Q et al. *ACS nano* **2013**, 7, 1487–94.



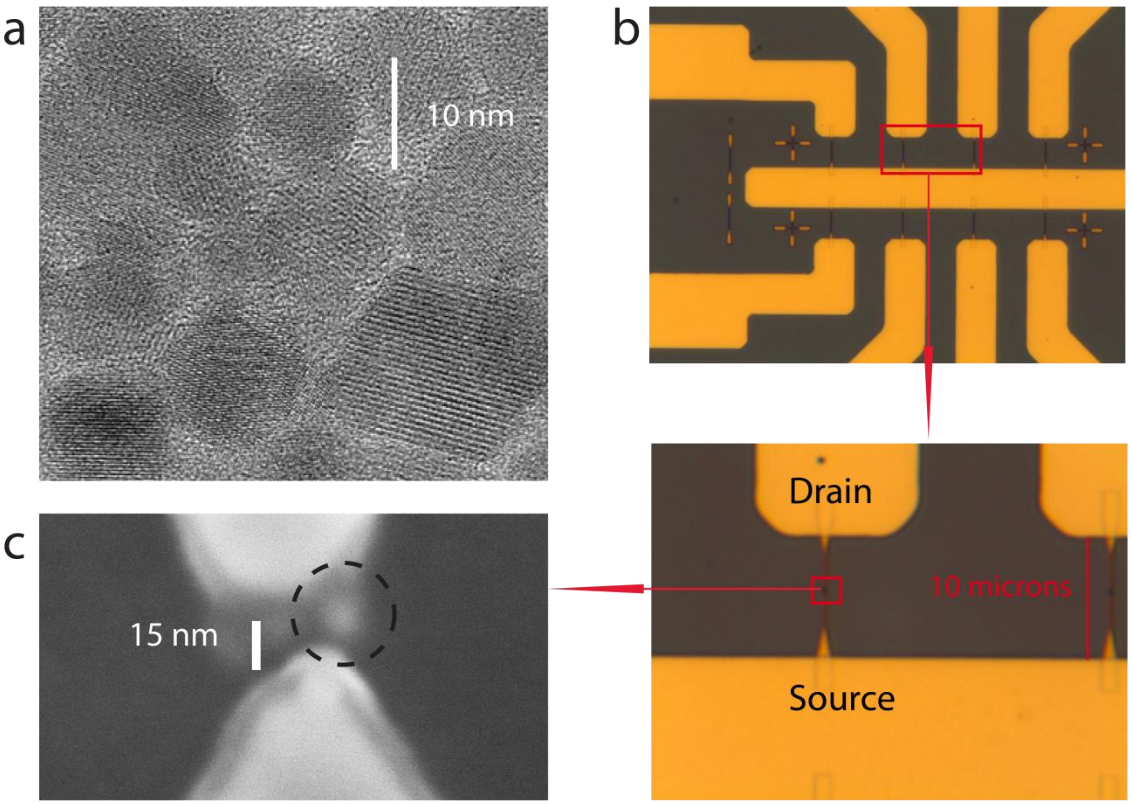
Verwey transition in magnetite (Fe_3O_4)

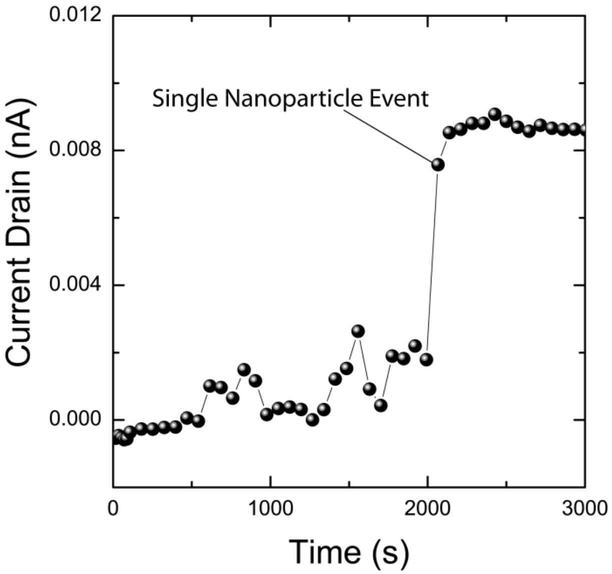




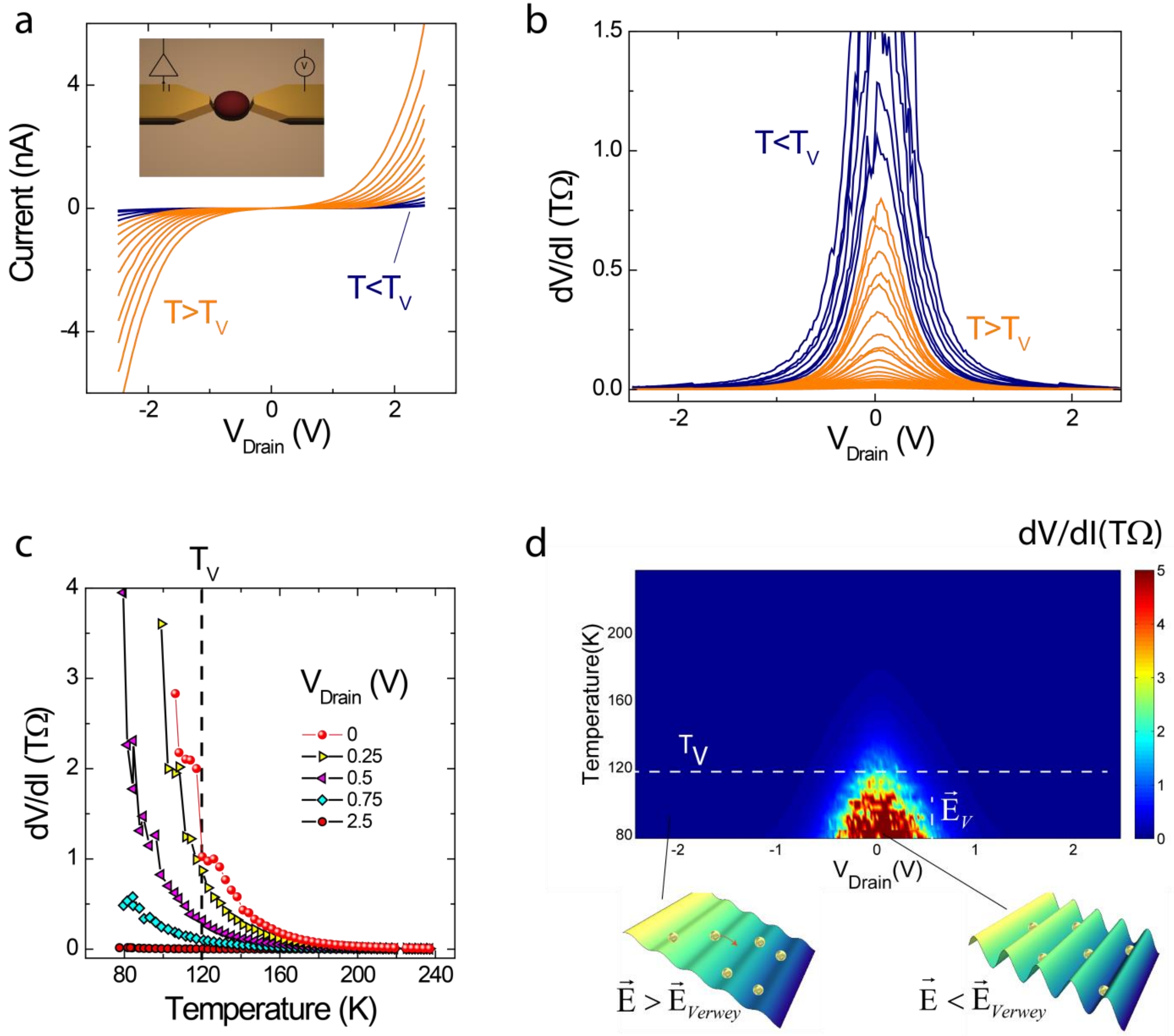


Verwey transition in single magnetite nanoparticles





Verwey transition in single magnetite nanoparticles



$d \simeq 15\ nm$

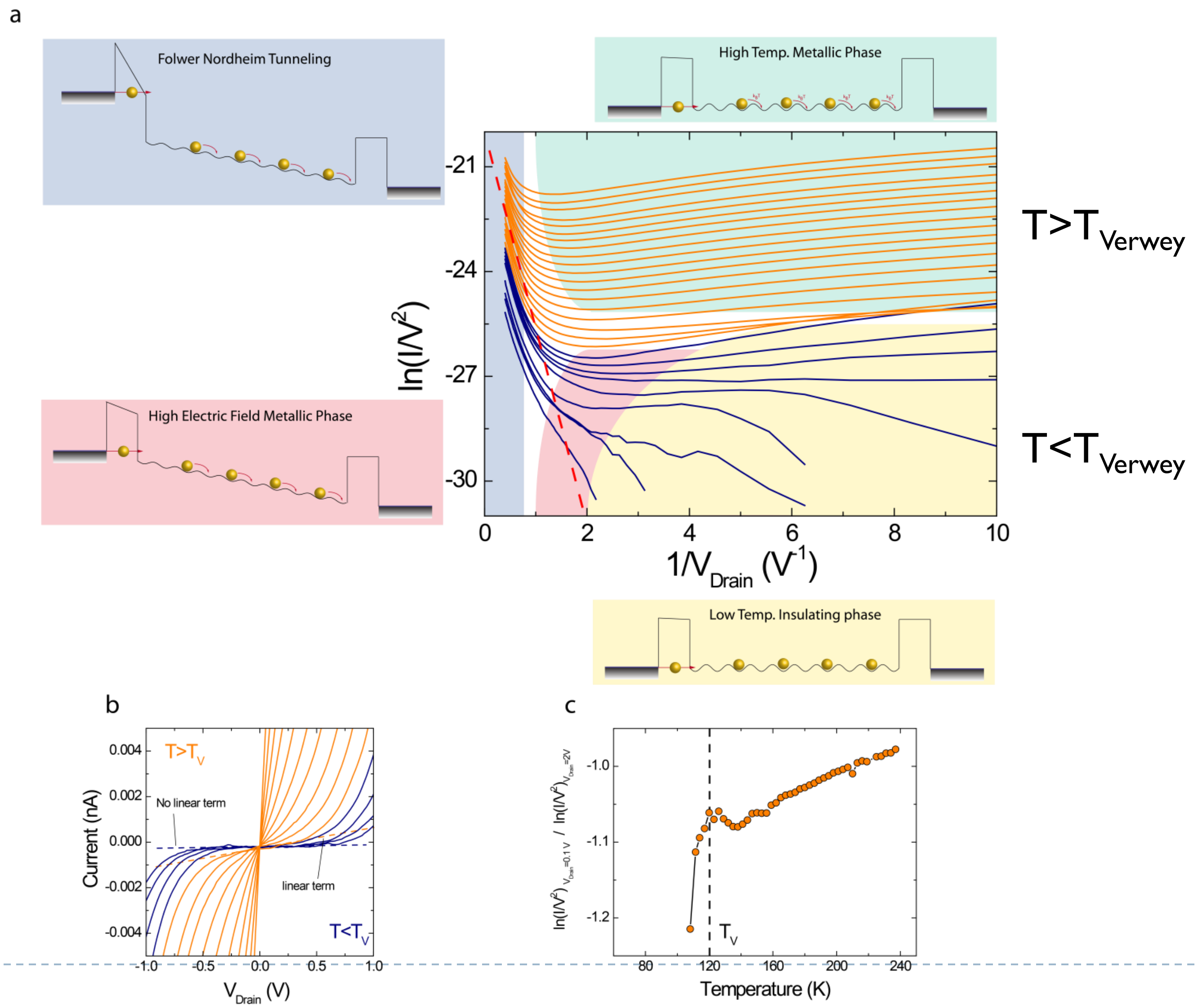
$|\vec{E}_V| = {}^{V_V}/_{d} = 3.3\ 10^5\ V\ cm^{-1}$

$a = 0.295\ nm$

potential depth :

$V_t = |\vec{E}_V| \times a \simeq 9.8\ meV.$

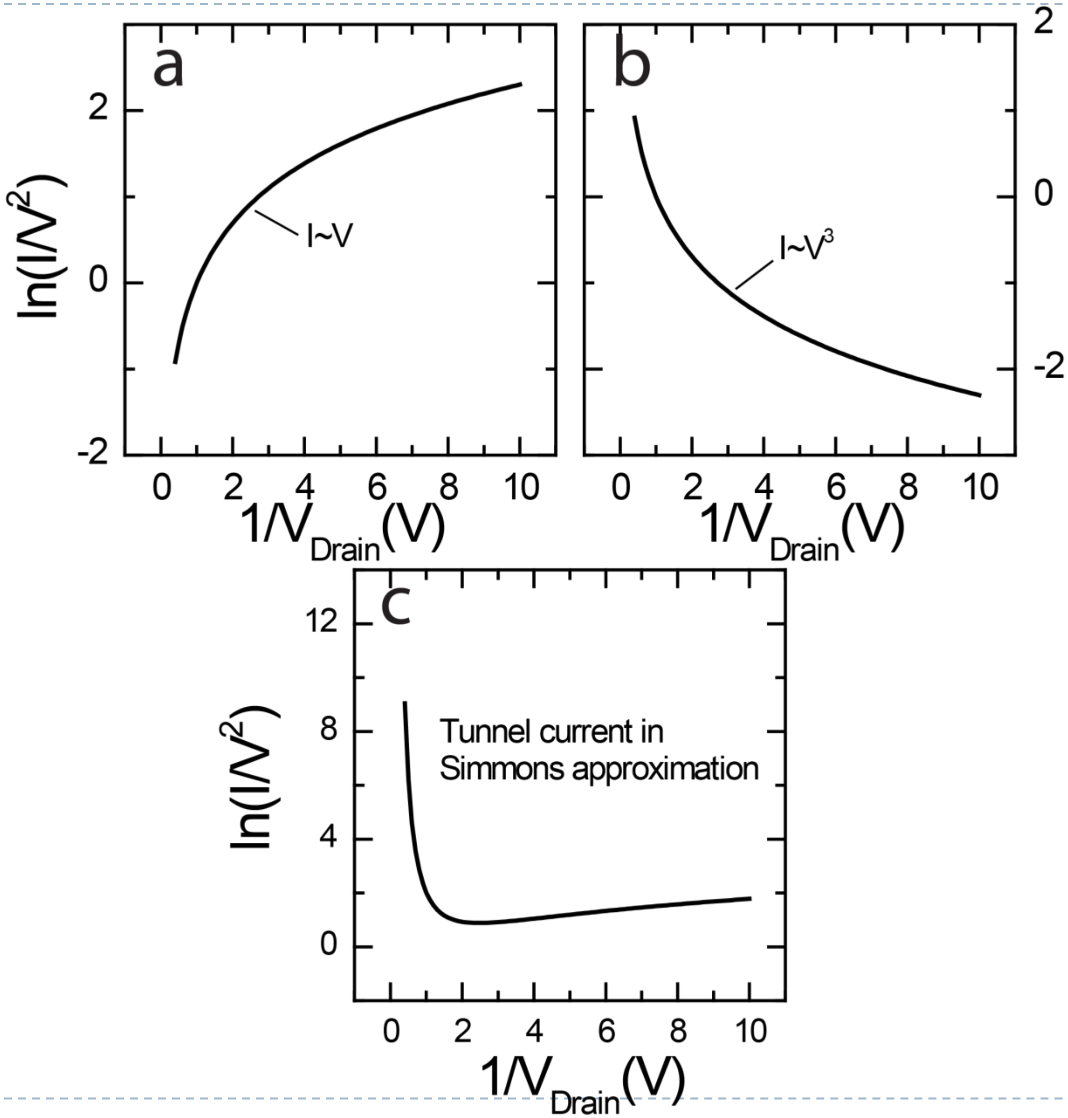
Folwer-Nordheim Plot



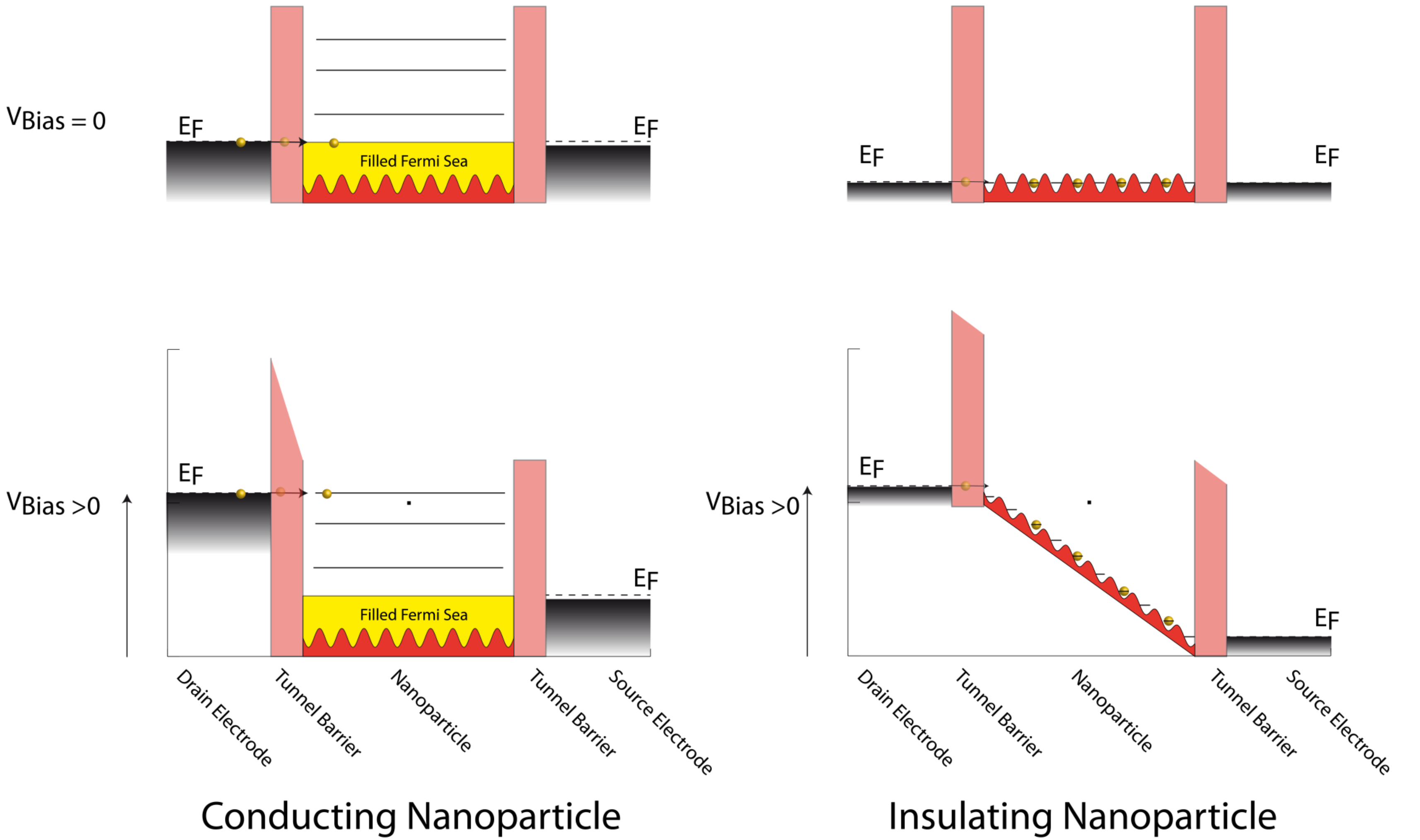
CONCLUSIONS

- Effective long distance hopping in metallic nanoparticles arrays is possible because of **cotunneling**
- **Efros-Shklovskii** laws applies in metallic nanoparticles arrays as a function of **temperature**, but also as function of **electric field**.
- A new projection method of preparing single nanoparticles devices
- Allows to study non-equilibrium Verwey transition in magnetite

Contributions to Folwer-Nordheim plot

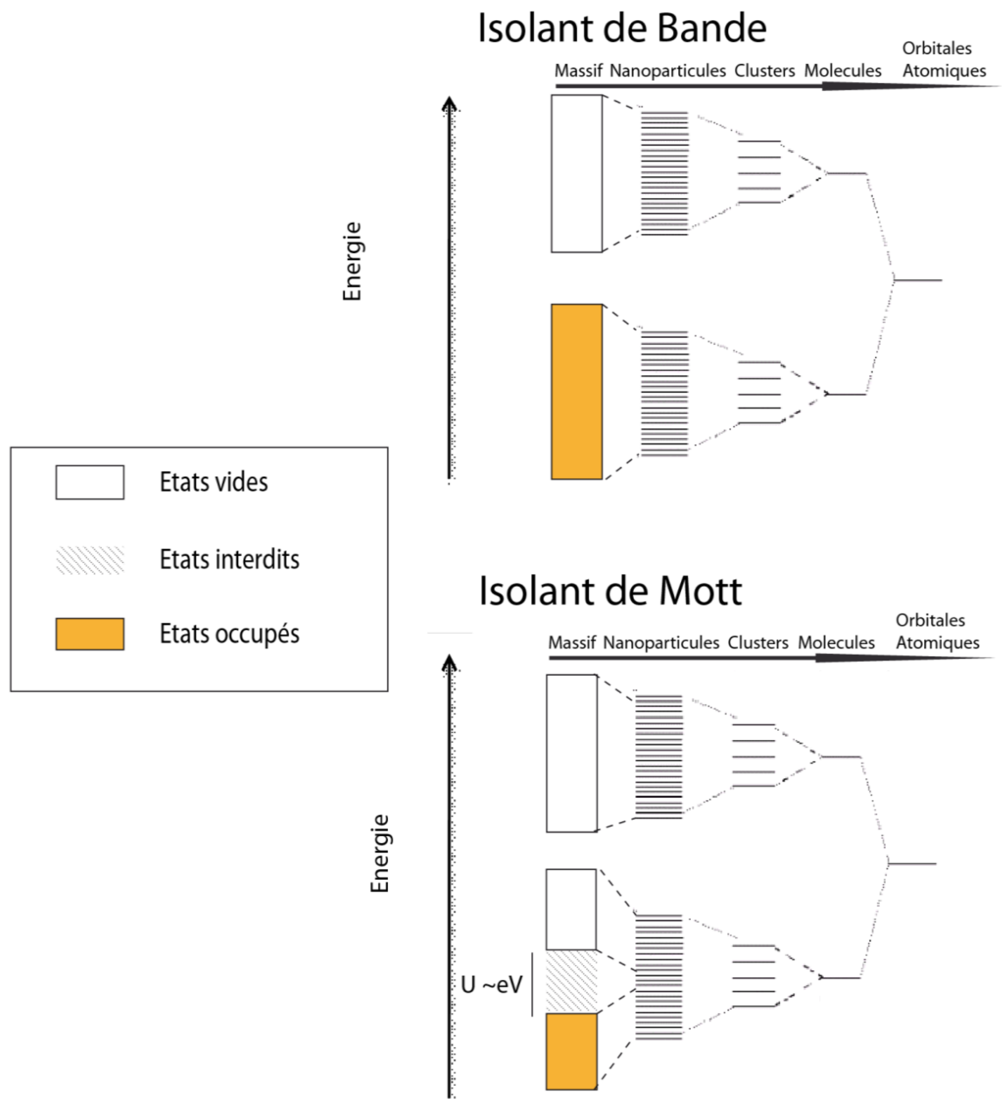


Verwey transition in single magnetite nanoparticles



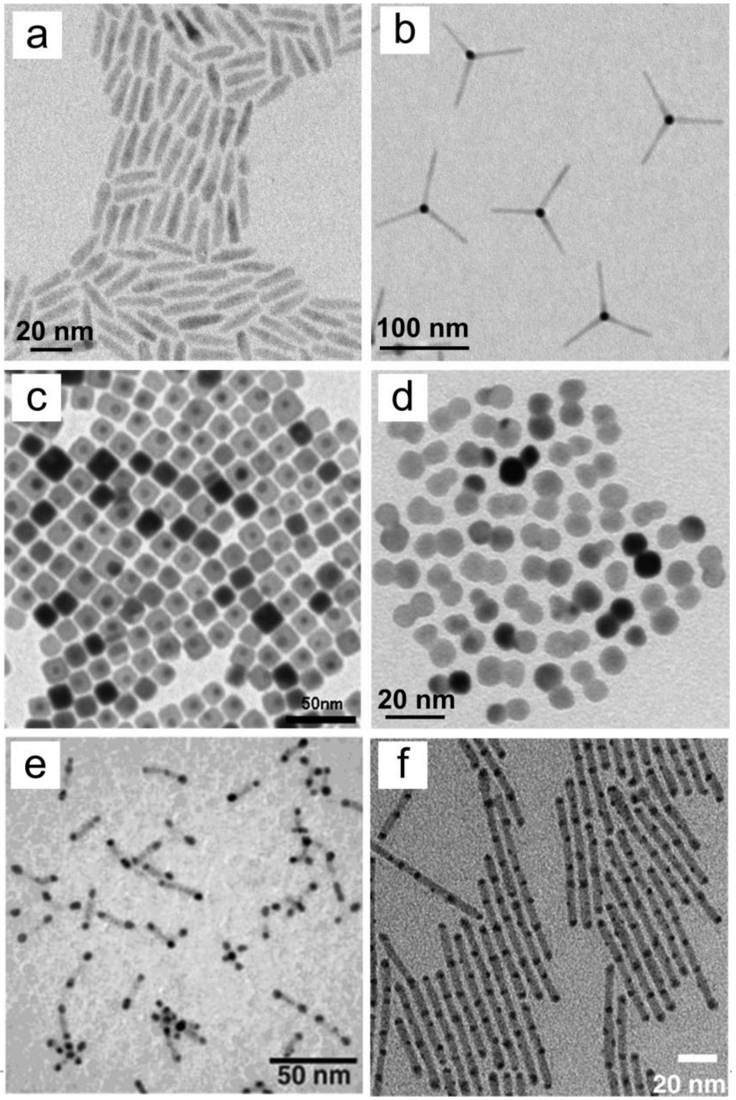
Tunneling spectroscopy of nanoparticles

- To study the construction of band structures with discrete electronic levels
  - Semi-conductors (strong quantum confinement effects)
  - Metals (fractal wave functions, random matric theory and relation with Anderson localization)
  - Semi-metals (no studies so far)
  - Mott Insulator (no studies so far)
  - Superconductors (only a few works)



A plethora of nanoparticles

(a) CdSe/CdS nanorods
(b) CdSe/CdS
(c) Au/PbS core-shells
(d) $CoPt_3$-Au dumbbells
(e) Au-CdSe-Au rods
(f) CdS-Au2S segmented nanoheterostructures.



Talapin et al.
*Chem. Rev. 2010, **110**, 389*

Electron transport in granular films (Ni-SiO_2) as function of electric field

Sheng, P. & Abeles, B.
Physical Review Letters **28**, 34-37(1972).

Acivated law as function of electric field

$$I = I_0 \exp(-E_{Coulomb} / eV)$$