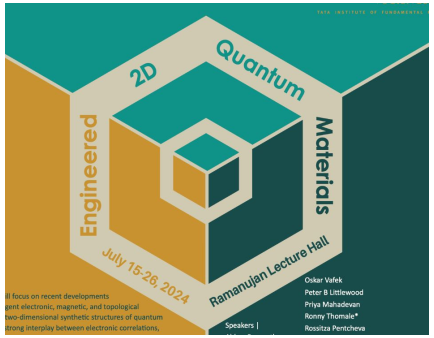

INTERNATIONAL CENTRE for THEORETICAL SCIENCES
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Engineering electron-phonon interactions in noble metals with nanoscale interfaces

Shreya Kumbhakar

IISc, Bangalore

INDIAN INSTITUTE OF SCIENCE
भारतीय विज्ञान संस्थान

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Prof. Anshu Pandey

Dr. T Phanindra Sai

Prof. Arindam Ghosh

Department of Physics, IISc Bangalore

Solid State Structural Chemistry Unit (SSCU), IISc Bangalore

शिक्षा मंत्रालय
MINISTRY OF EDUCATION
सत्यमेव जयते

CeNSE
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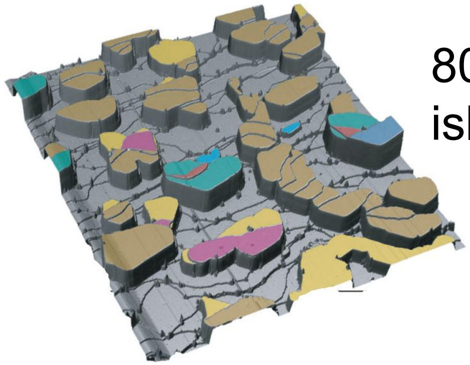
Modulating electron-phonon interaction in metals

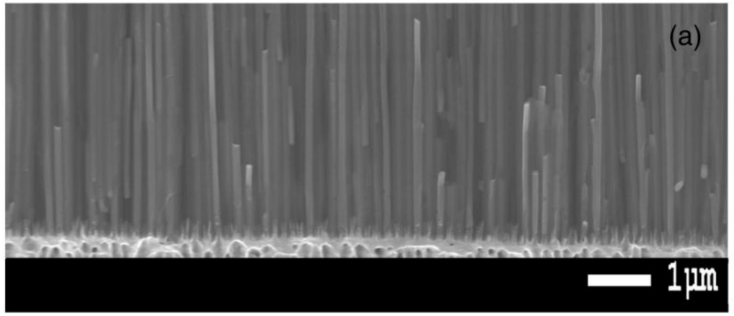
Aligning states in a quantum well with fermi level



800 nm^2 Pb islands on Cu

Phys. Rev. Lett. ***114***, *047002*

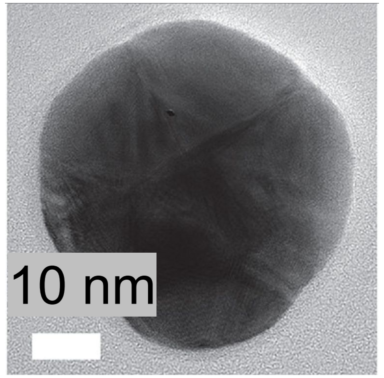
Achieving low-frequency phonons with surfaces



50 nm Sn nanowires

Phys. Rev. B 99, 064512

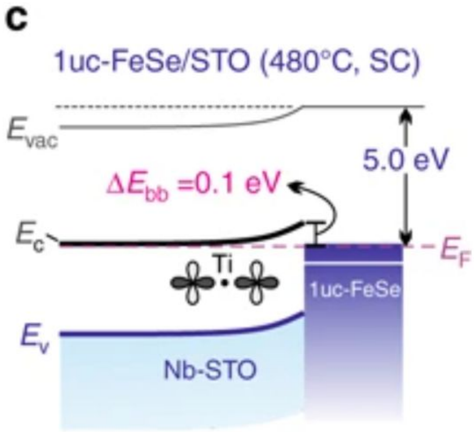
Electron scattering from surfaces



Polycrystalline Au nanoparticles

ACS Photonics 2021, 8, 3, 752–757

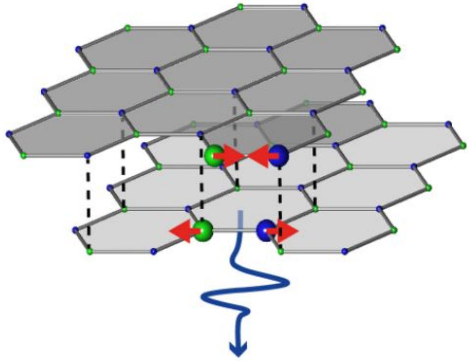
Interfacial el-ph interaction



$SrTiO_3$ on FeSe

Nat Commun ***8***, *214 (2017)*

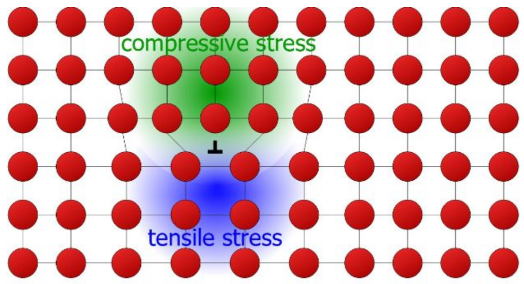
Optically driving the lattice



THz spectroscopy in bilayer graphene

Phys. Rev. B 95, 024304

Stress

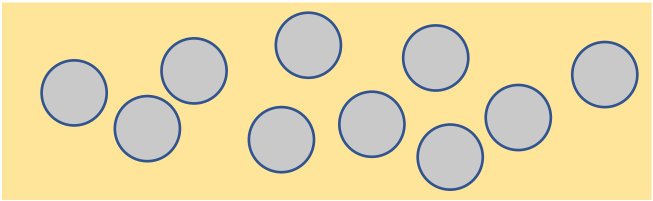


Proc. Natl. Acad. Sci. 2014, 111, 8712–8716

Our approach

Dense network of nanoscale crystalline interfaces

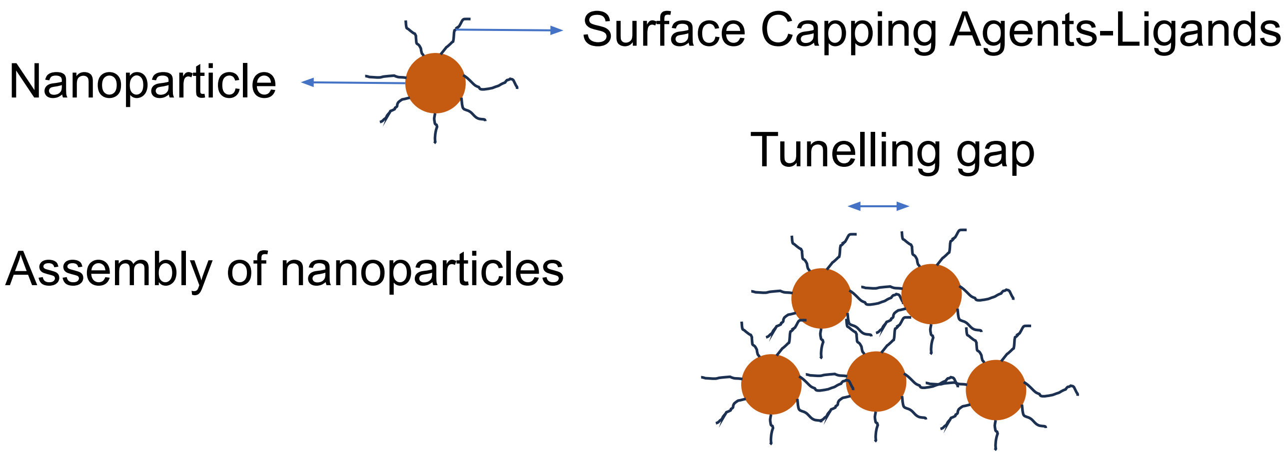
Metal nanoparticles embedded inside a metallic matrix

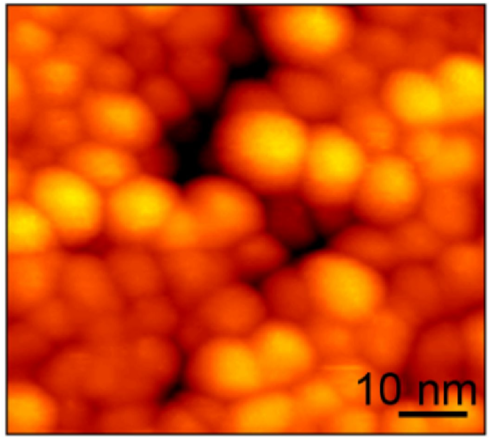


Challenge

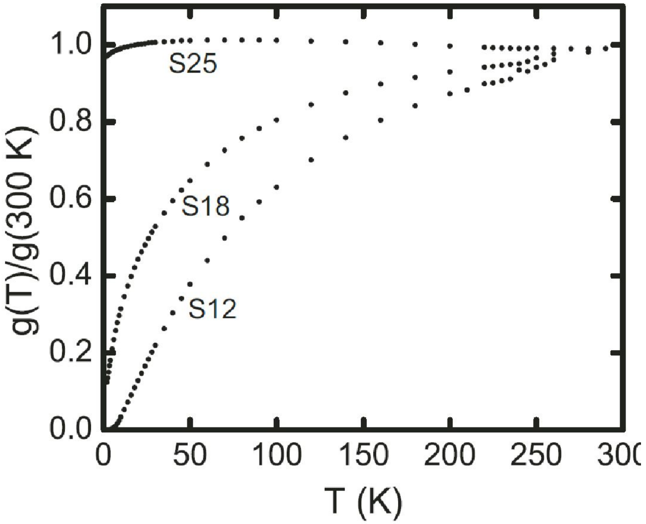
Not achieved: Bottom-up assembly of ‘Metal’ with nanoparticles

<u>Electron tunneling effects</u>: Coulomb blockade, Variable Range hopping, Activated transport



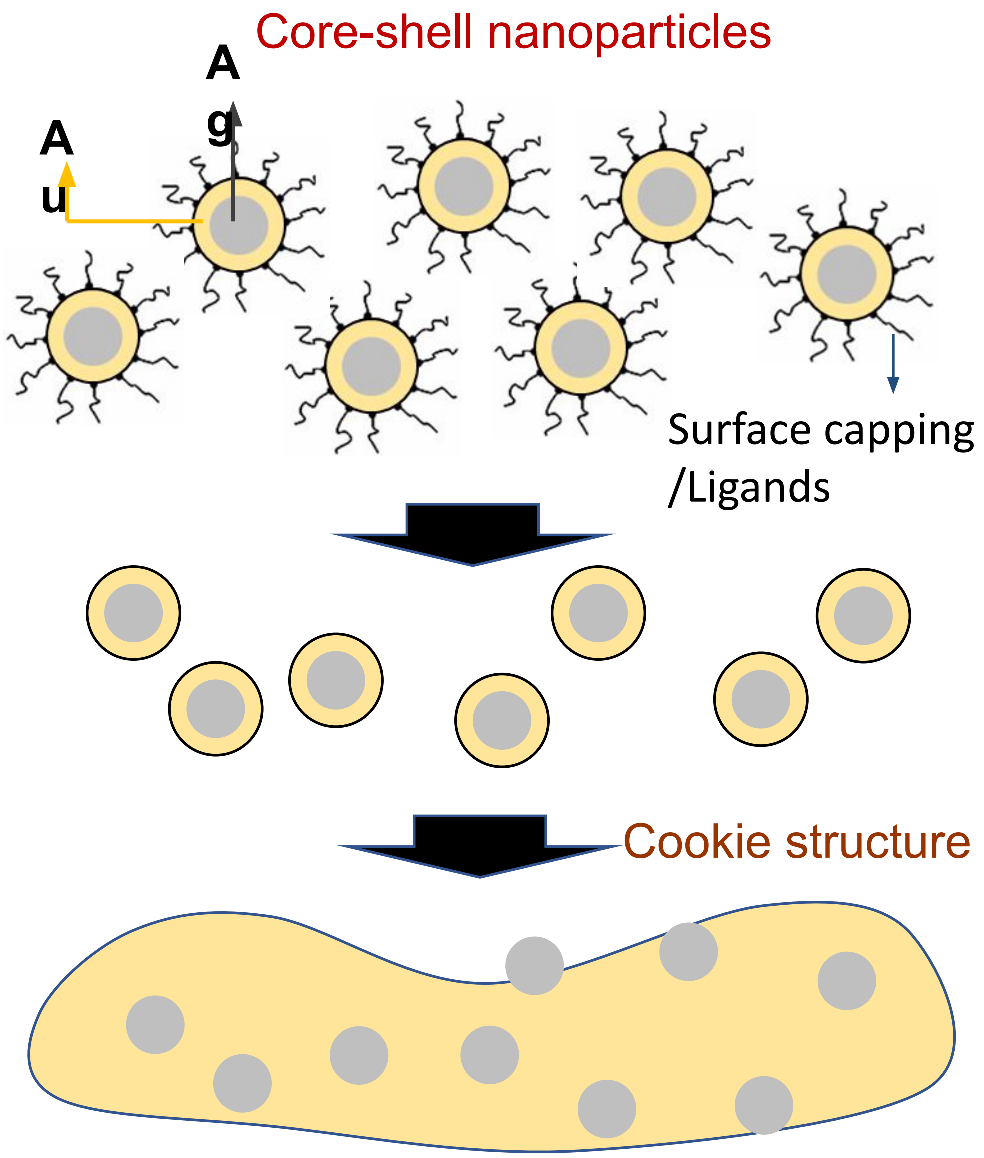


Au nanoparticles



Phys .Rev. B 89, 155117 (2014)

Our approach: A bi-metallic nano-hybrid

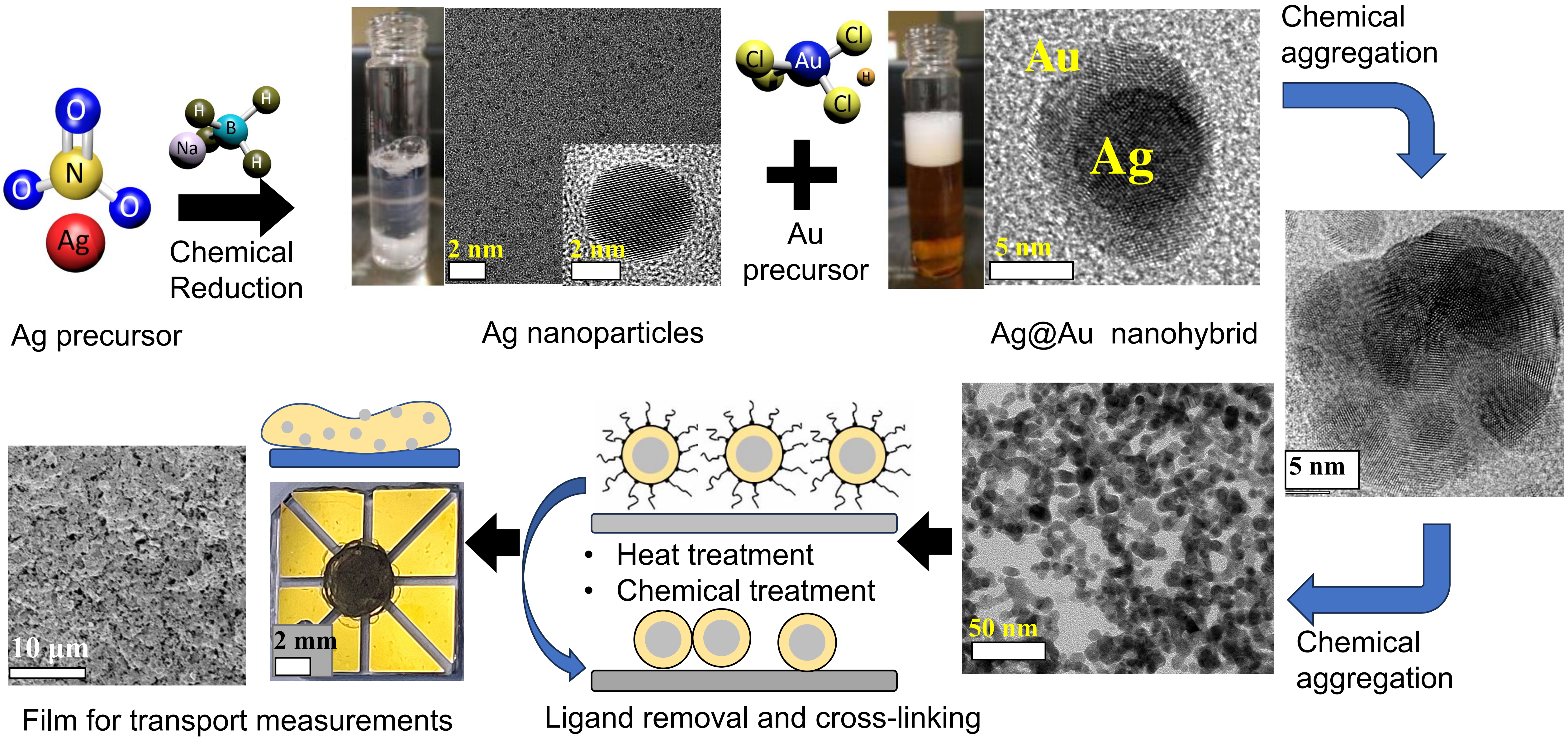


Near identical lattice constants of Au and Ag : 4.078 Å and 4.085 Å

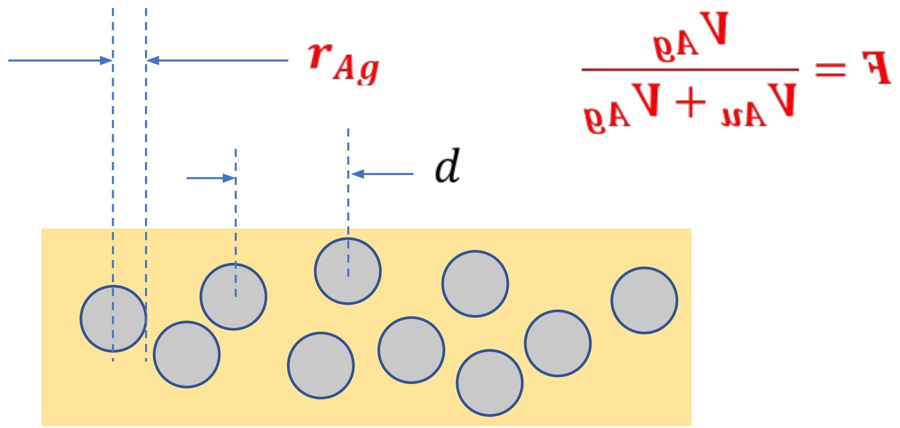
Chemical route – The process flow

ACS Appl. Electron. Mater. 2023, 5, 5, 2893−2901

Ag(NP) – Au hybrid

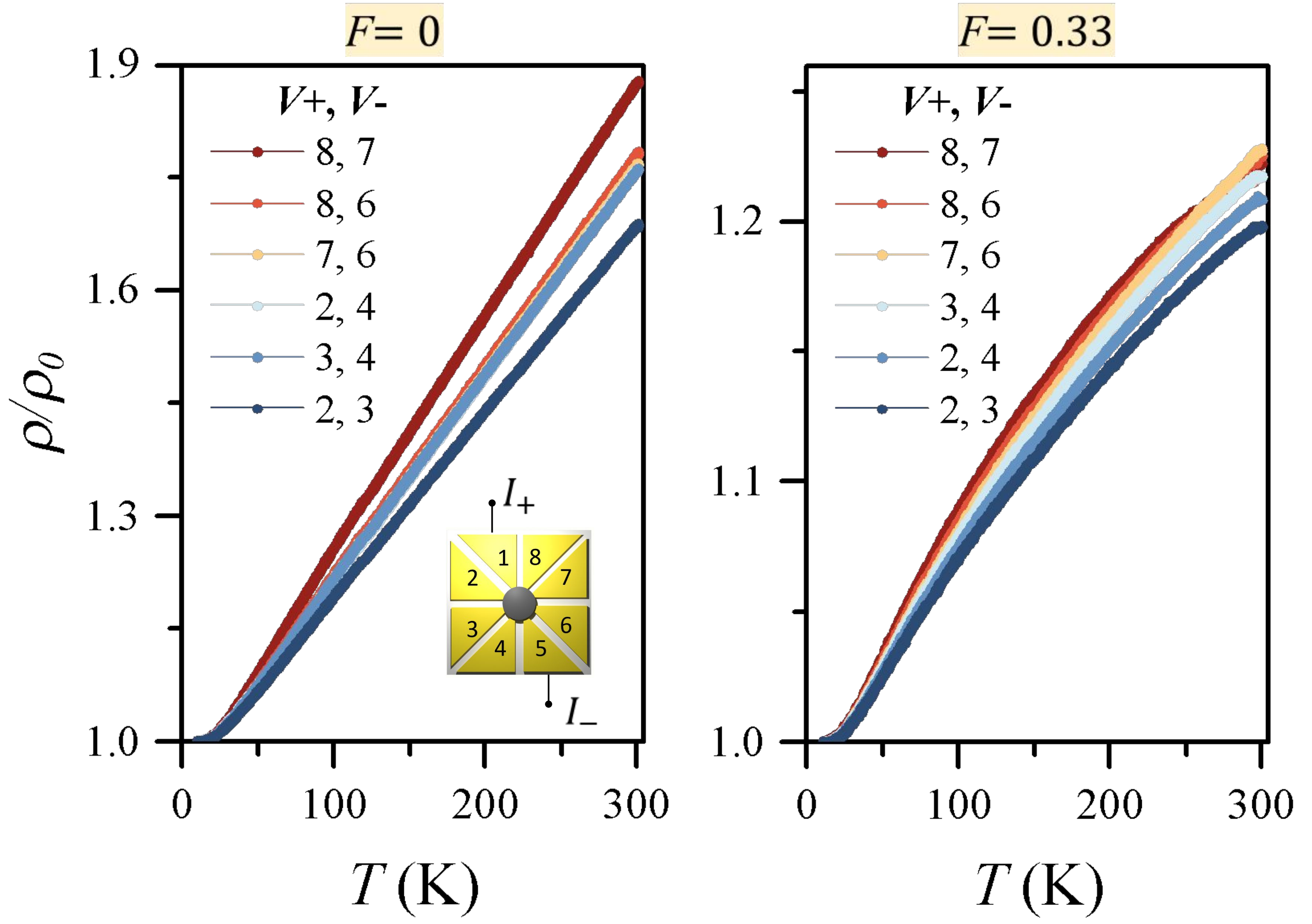


Temperature-dependance of electrical resistivity



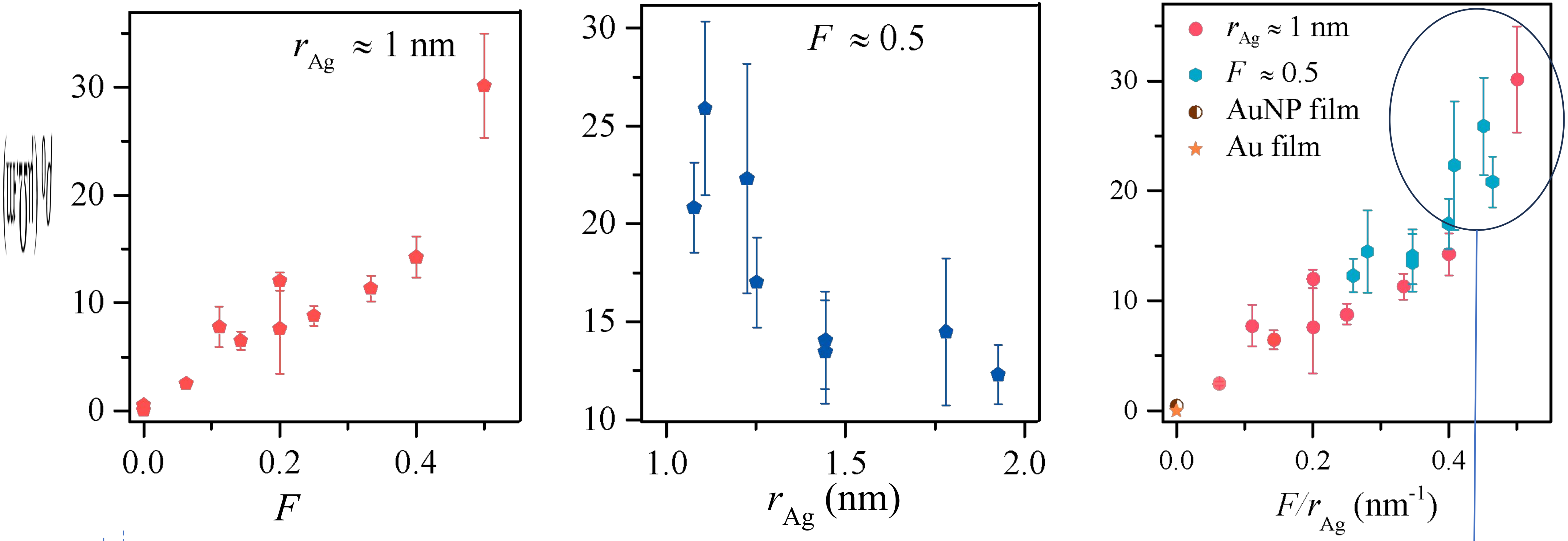
- r_{Ag}: AgNP radius ~ 1 – 3 nm
- d: AgNP distance ~ 3 – 6 nm

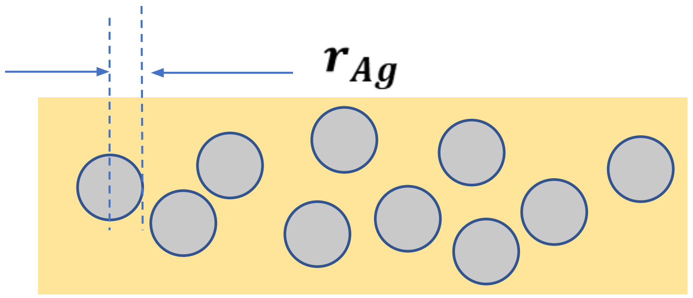
- Homogenous metallic transport
- Saturation of resistivity for $F > 0$



Resistivity – interface correlation

ρ_0: Resistivity at base temperature ~6 K





$$F = \frac{V_{Ag}}{V_{Au} + V_{Ag}}$$

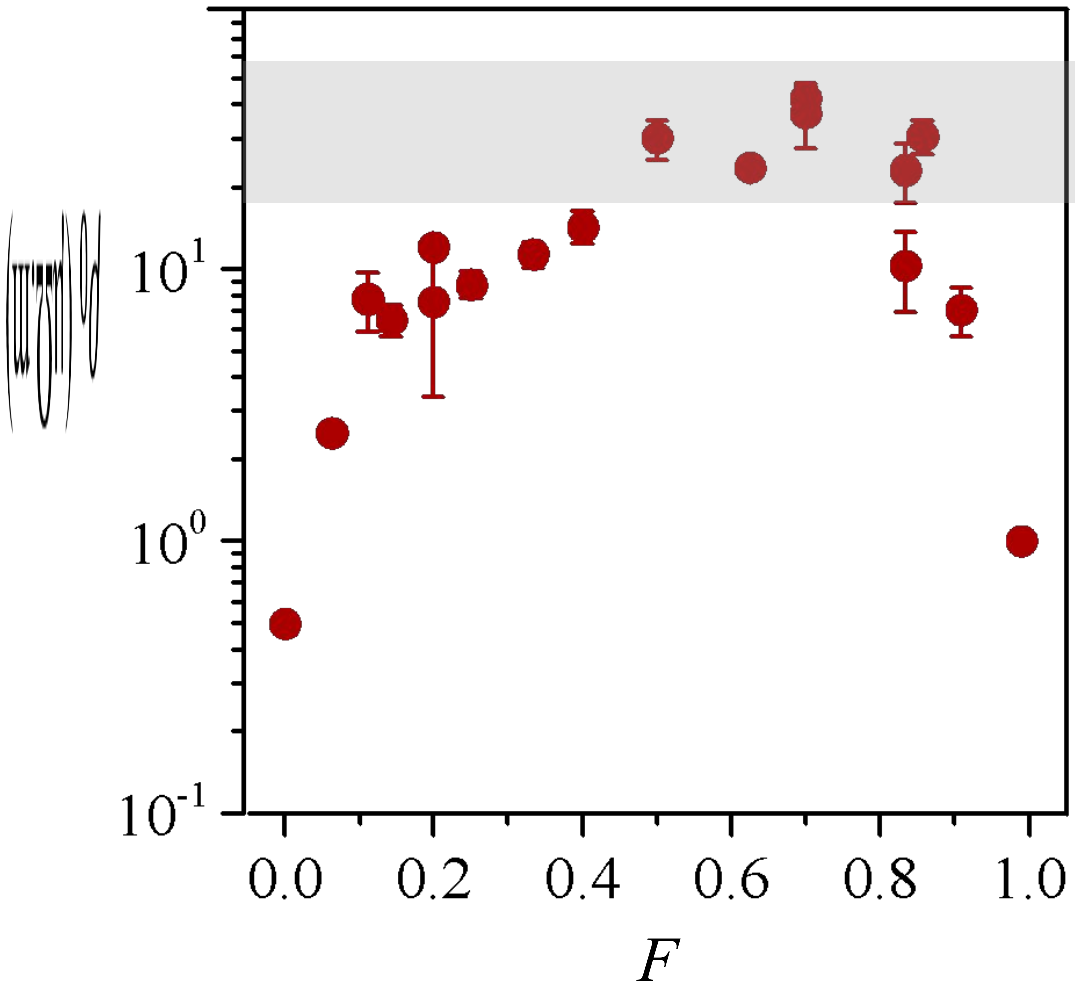
Interface area of Ag per unit volume: F/r_{Ag}

Increasing residual resistivity with overall interface area of Ag

Mott-Ioffe-Regel limit!

The Mott-Ioffe-Regel (MIR) Limit and ‘bad metals’

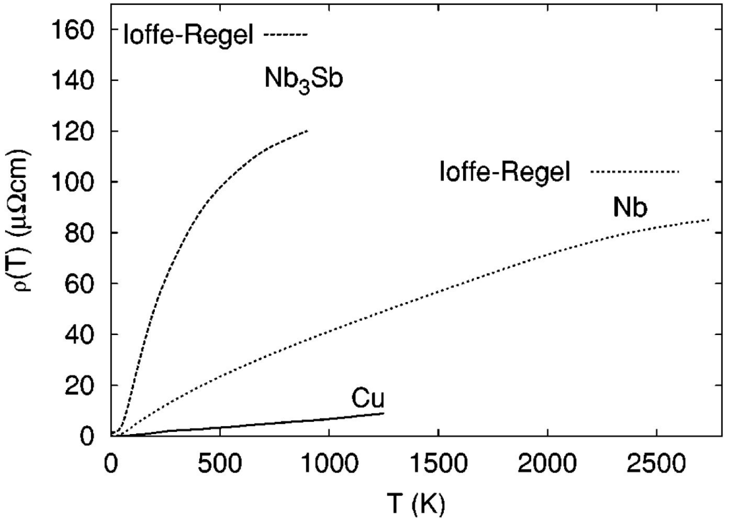
$$F = \frac{V_{Ag}}{V_{Au} + V_{Ag}}$$



MIR Limit: $k_F l = 1$ $\rho_{MIR}^{Au} = 24.6\ \mu\Omega\text{-m}$

$$\rho_{MIR} = \frac{3\pi^2\hbar}{e^2 k_F (k_F l)} = \frac{3\pi^2\hbar}{e^2 k_F}$$

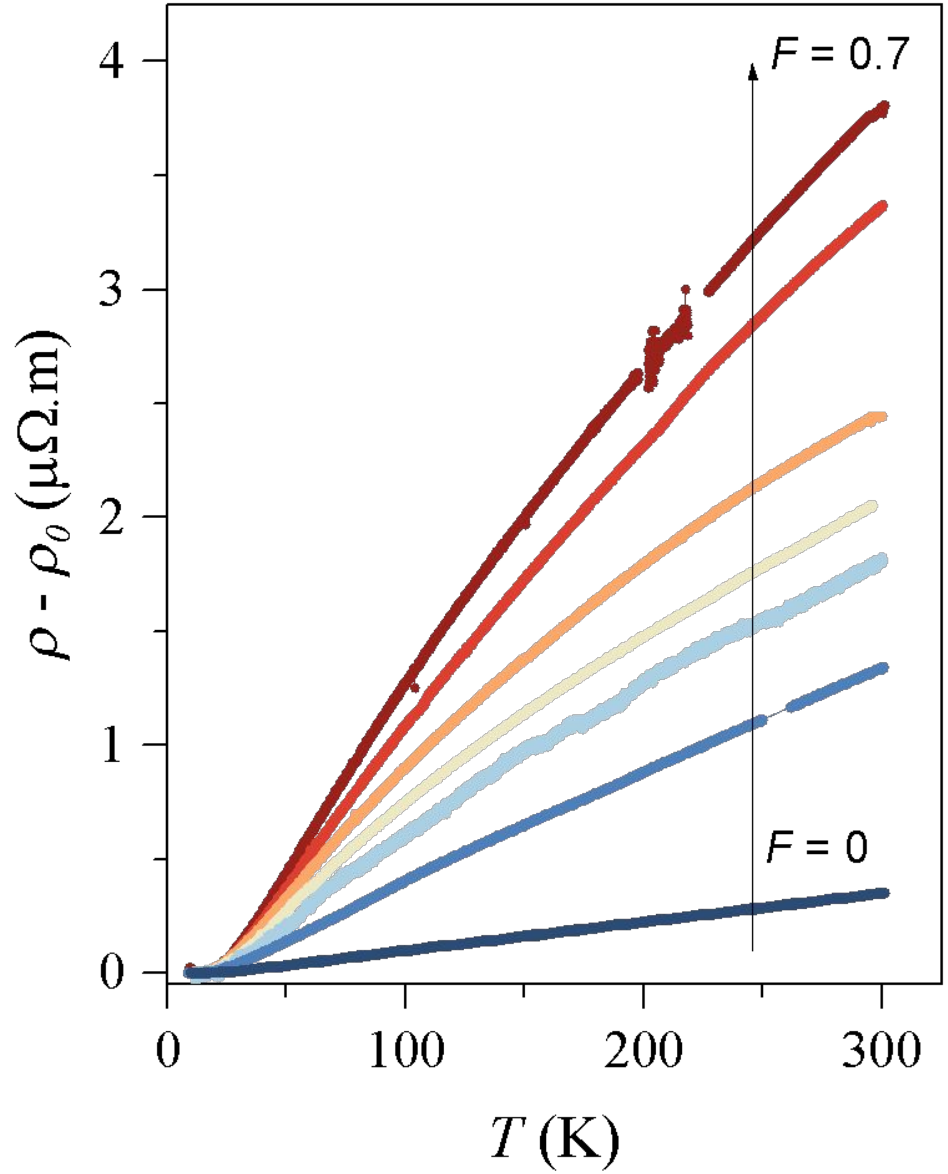
- **Mean-free path approaching inter-atomic distance**
- **Ill-defined quasiparticles**



Gunnarsson, Calandra, Han Rev Mod Phys 2003 75, 1085

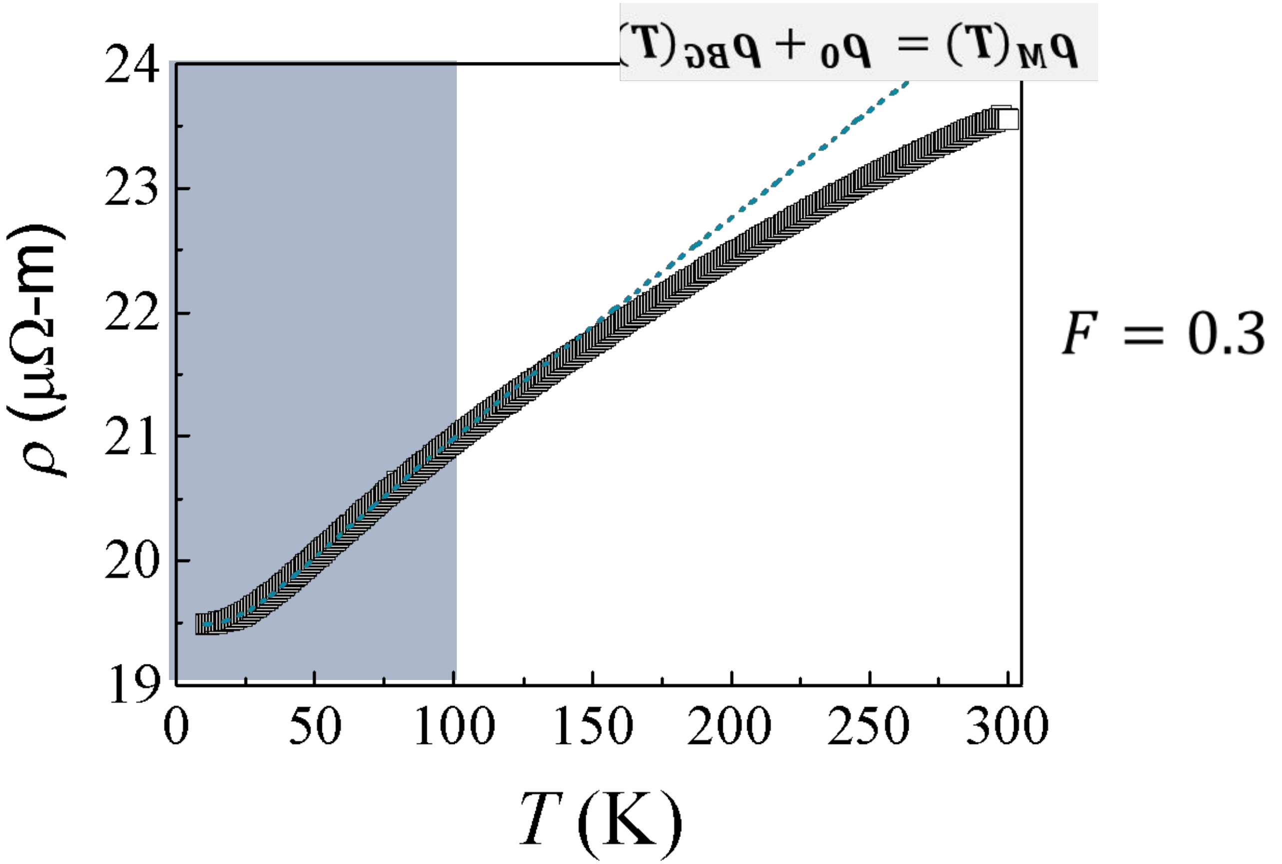
Resistivity saturation

The Mott-Ioffe-Regel (MIR) Limit and 'bad metals'



Conventional metallic transport in 'good' metals:
Bloch Gruneissen form of electron-phonon coupling:

$$\rho = \rho_0 + \rho_{BG}\ [\rho_{BG}(T) = \frac{2\pi k_B \lambda T}{\left(\frac{n}{m}\right) e^2} \left(\frac{T}{T_D}\right)^5 \int_0^{T_D/T} \frac{x^5}{(e^x-1)(1-e^{-x})} dx]$$



Resistivity saturation

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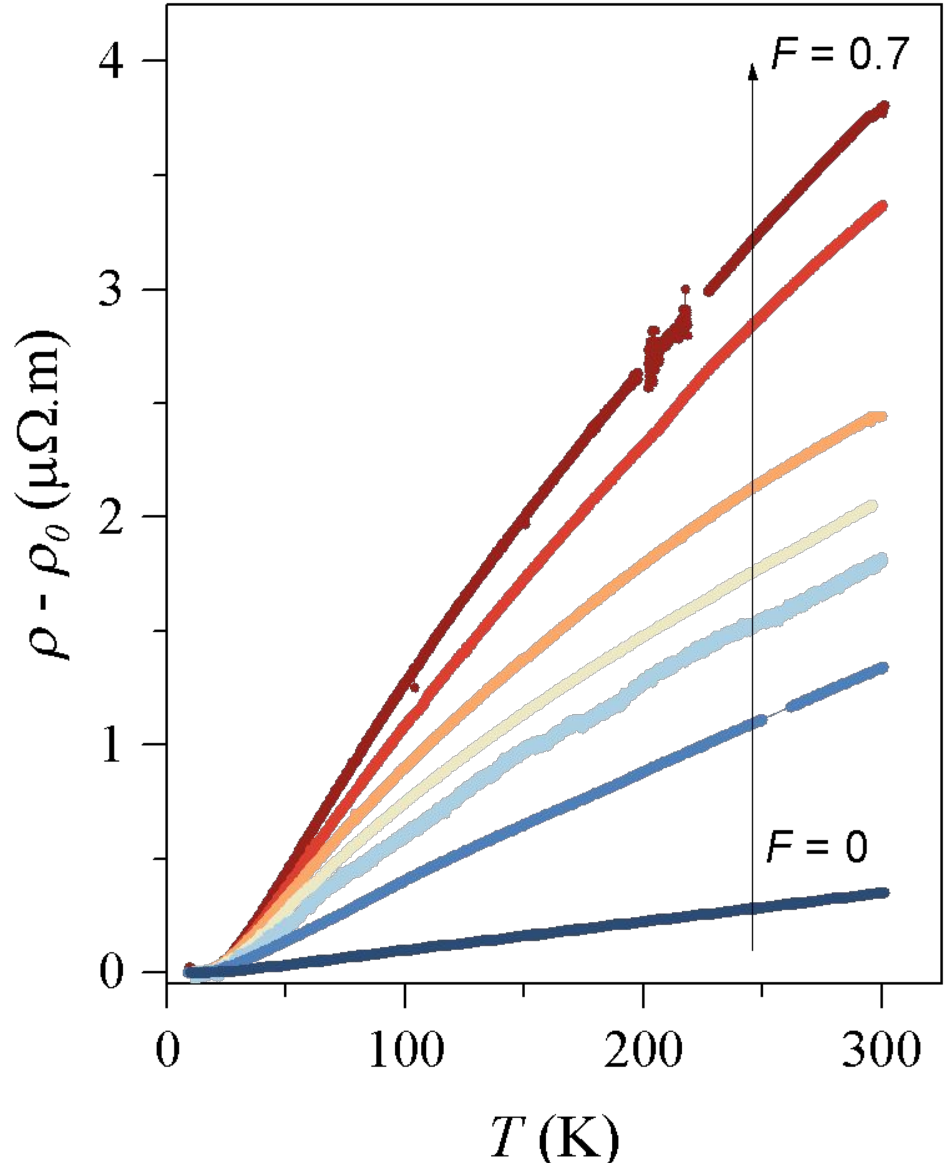
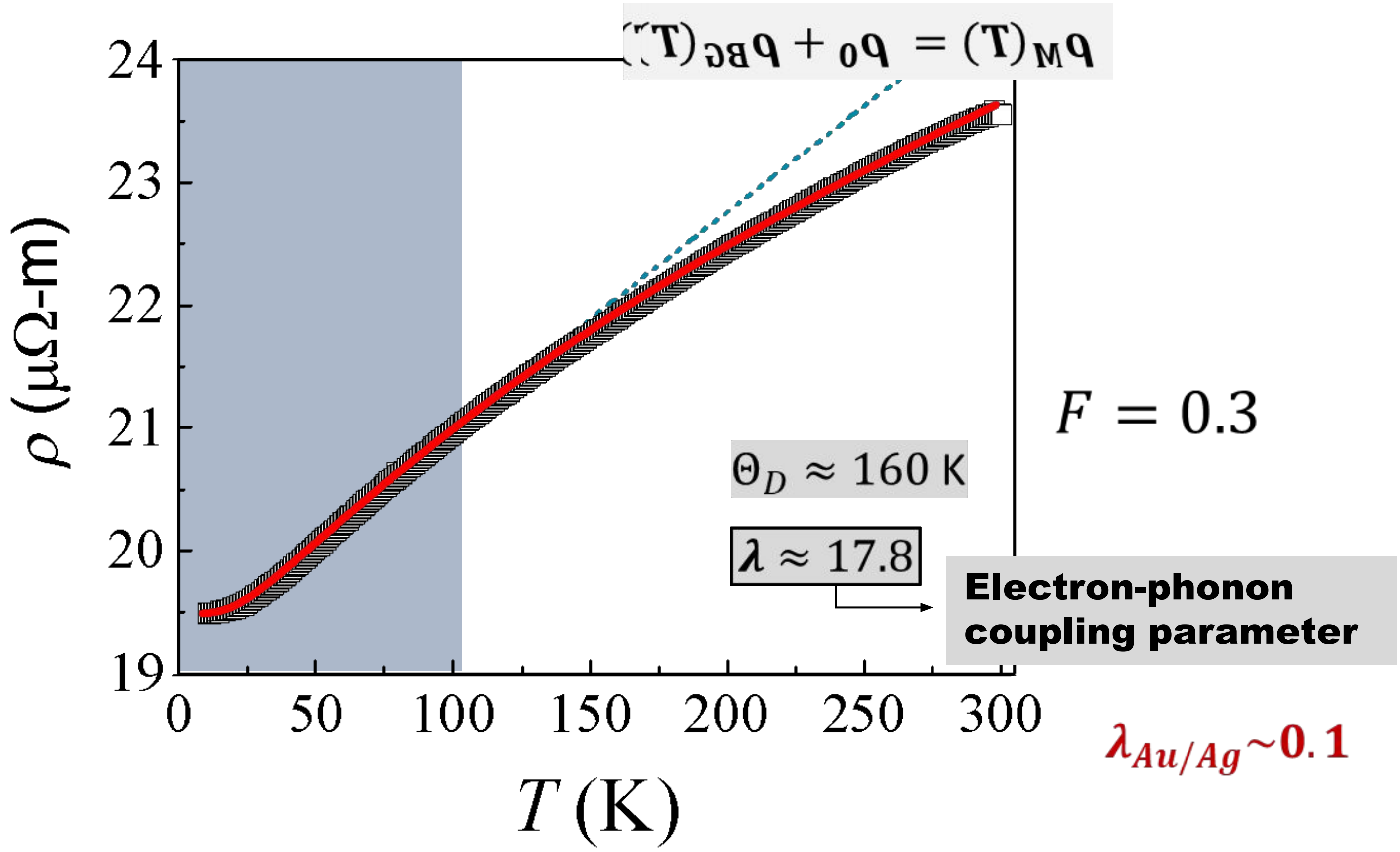


Two-channel transport

$$\frac{1}{\rho(T)-\rho(0)} = \frac{1}{\rho_{BG}} + \frac{1}{\rho_{\parallel}}$$

- $\rho_{\parallel} \sim \rho_{MIR}$



$F = 0.3$

$\lambda_{Au/Ag} \sim 0.1$

Point-contact spectroscopy – A primer

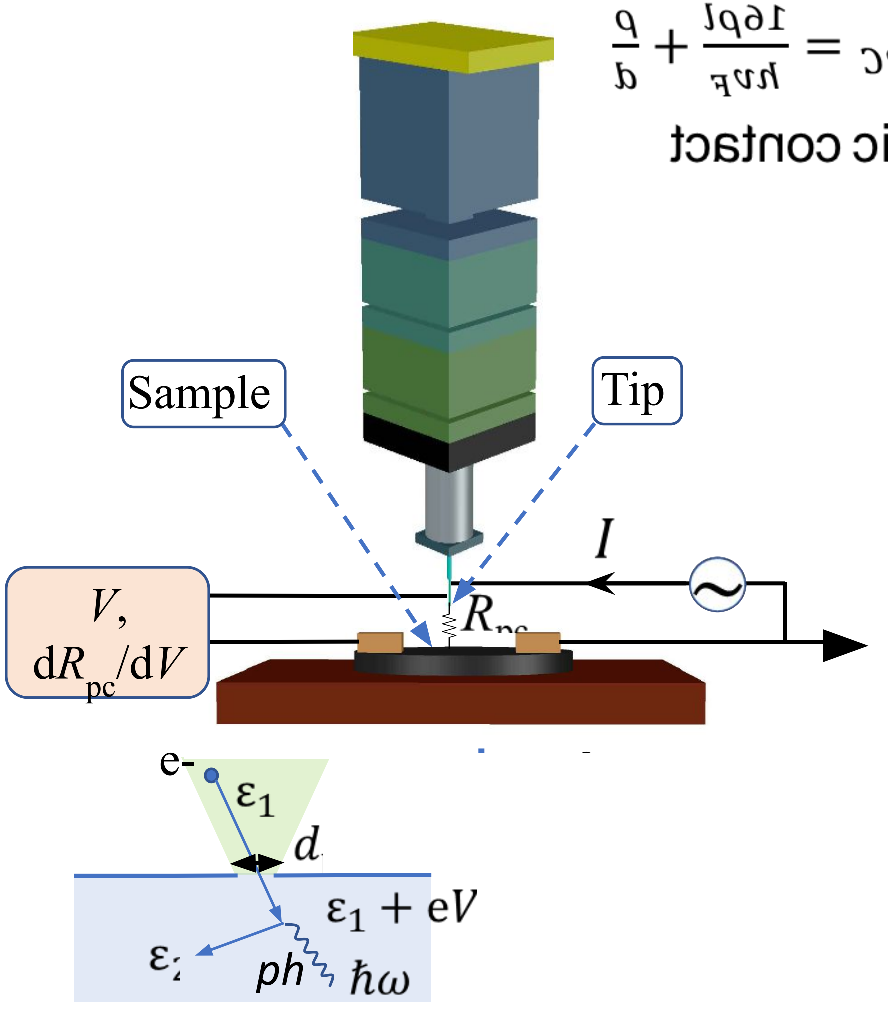
➤ Resistance at the point-contact: $R_{pc} = \frac{16\rho l}{\hbar v_F} + \frac{\rho}{d}$

➤ $\frac{1}{R_0}\frac{dR_{pc}}{dV} \approx \frac{8ed\rho_{pc}}{3\hbar v_F}\left(g(eV)\right)$ Ballistic contact

Migdal-Eliashberg function

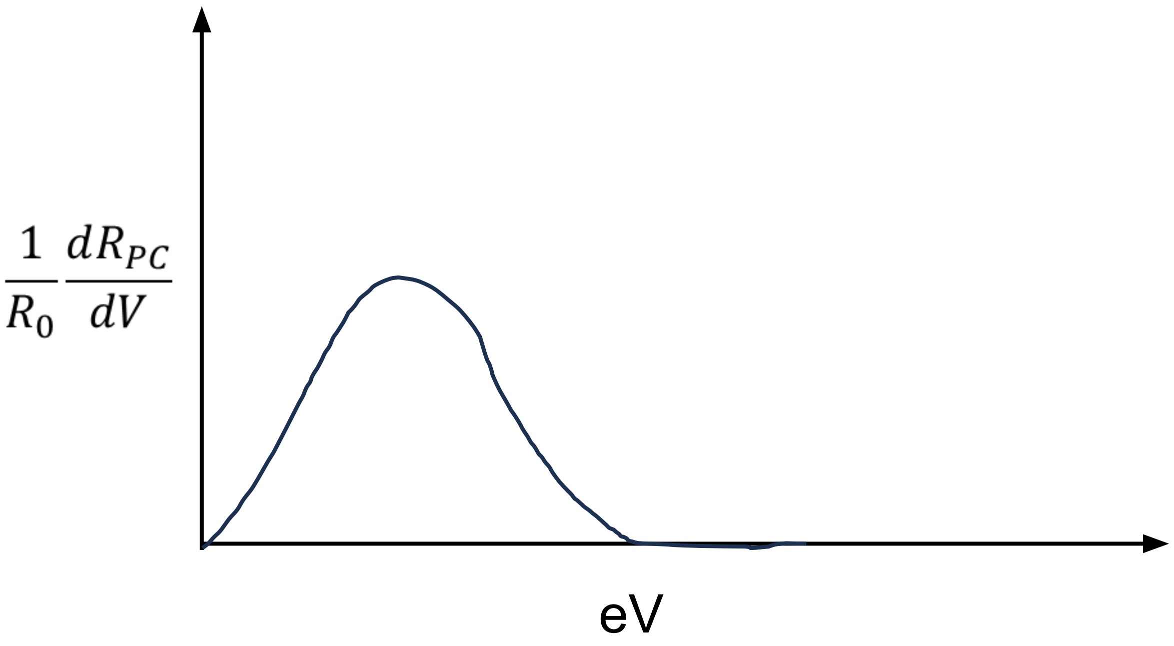
- Resembles Phonon DOS

Electron phonon coupling constant: $\lambda = 2\int_0^{\infty}\frac{g(\epsilon)}{\epsilon}d\epsilon$



$l >> d_{pc}$

Ballistic



Point-contact spectroscopy – A primer

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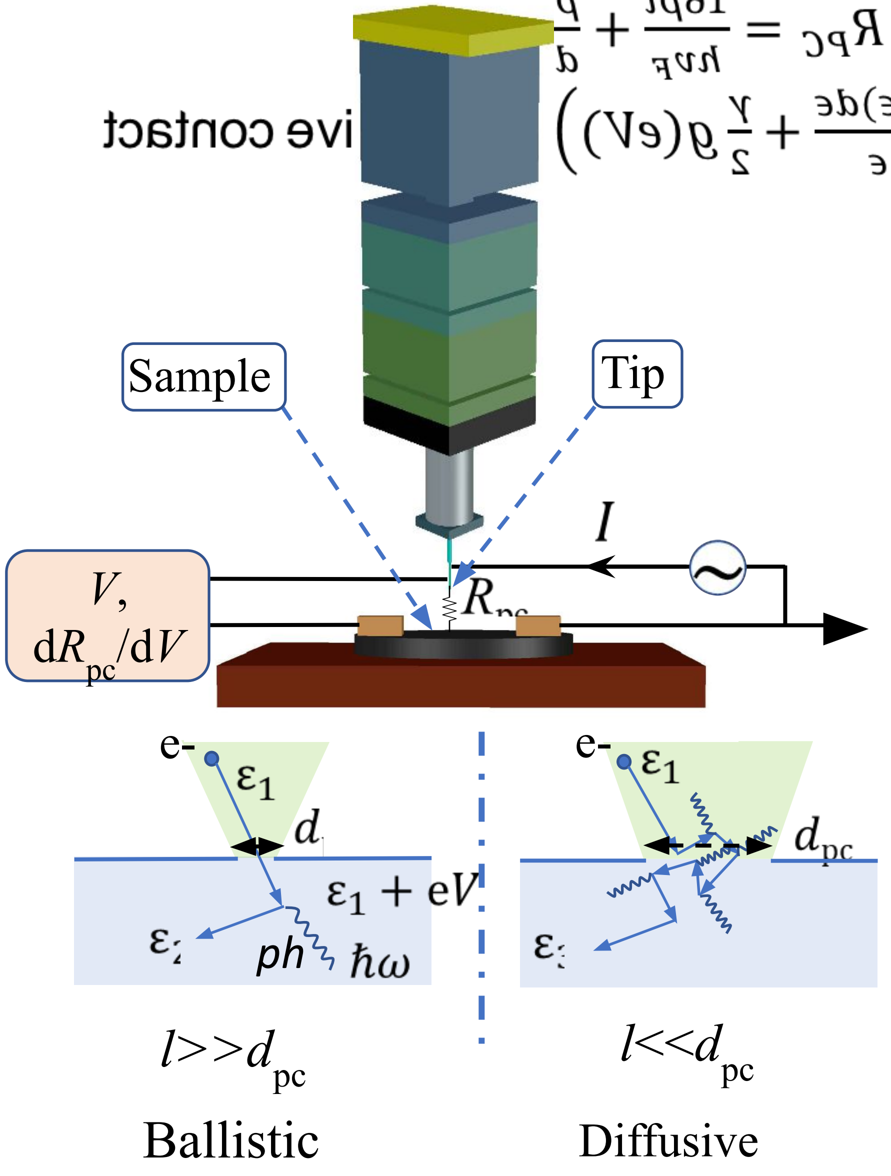
➢ $\frac{1}{R_0}\frac{dR_{pc}}{dV} \approx \frac{8ed_{pc}}{3\hbar v_F}\left(g(eV) + \gamma\int_0^{eV}\frac{g(\epsilon)}{\epsilon}d\epsilon + \frac{\gamma}{2}g(eV)\right)$



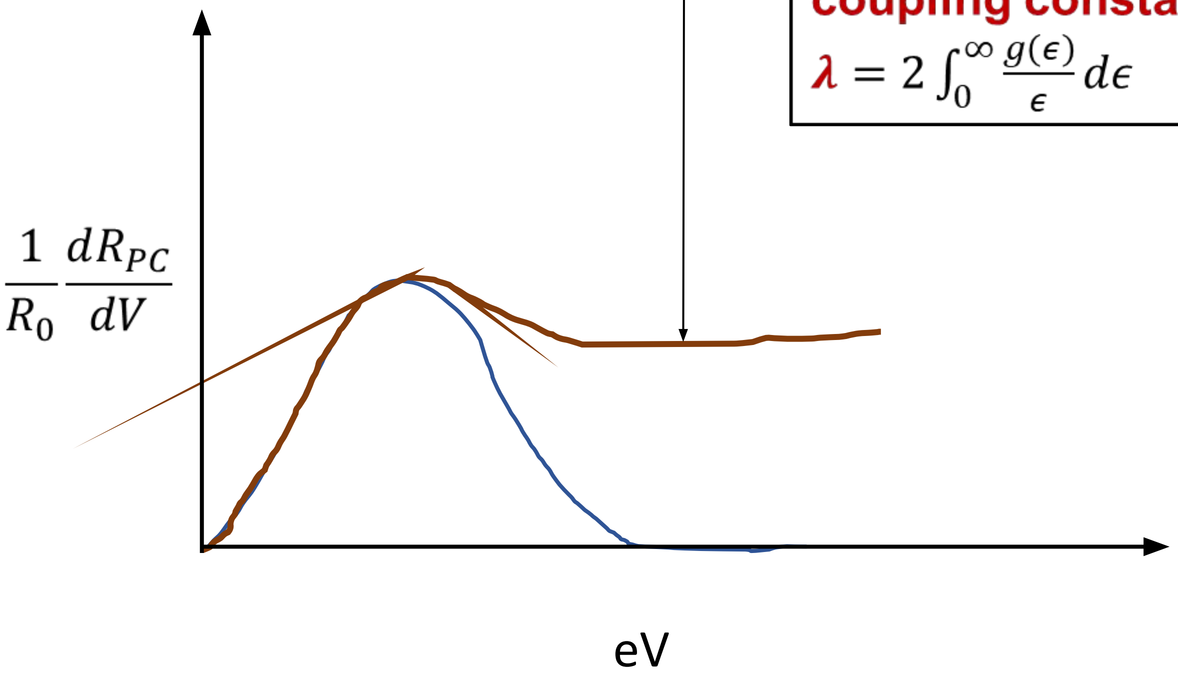
Migdal-Eliashberg function

- Resembles Phonon DOS

Background

Electron phonon coupling constant:

$\lambda = 2\int_0^\infty \frac{g(\epsilon)}{\epsilon}d\epsilon$



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Migdal-Eliashberg function — Background

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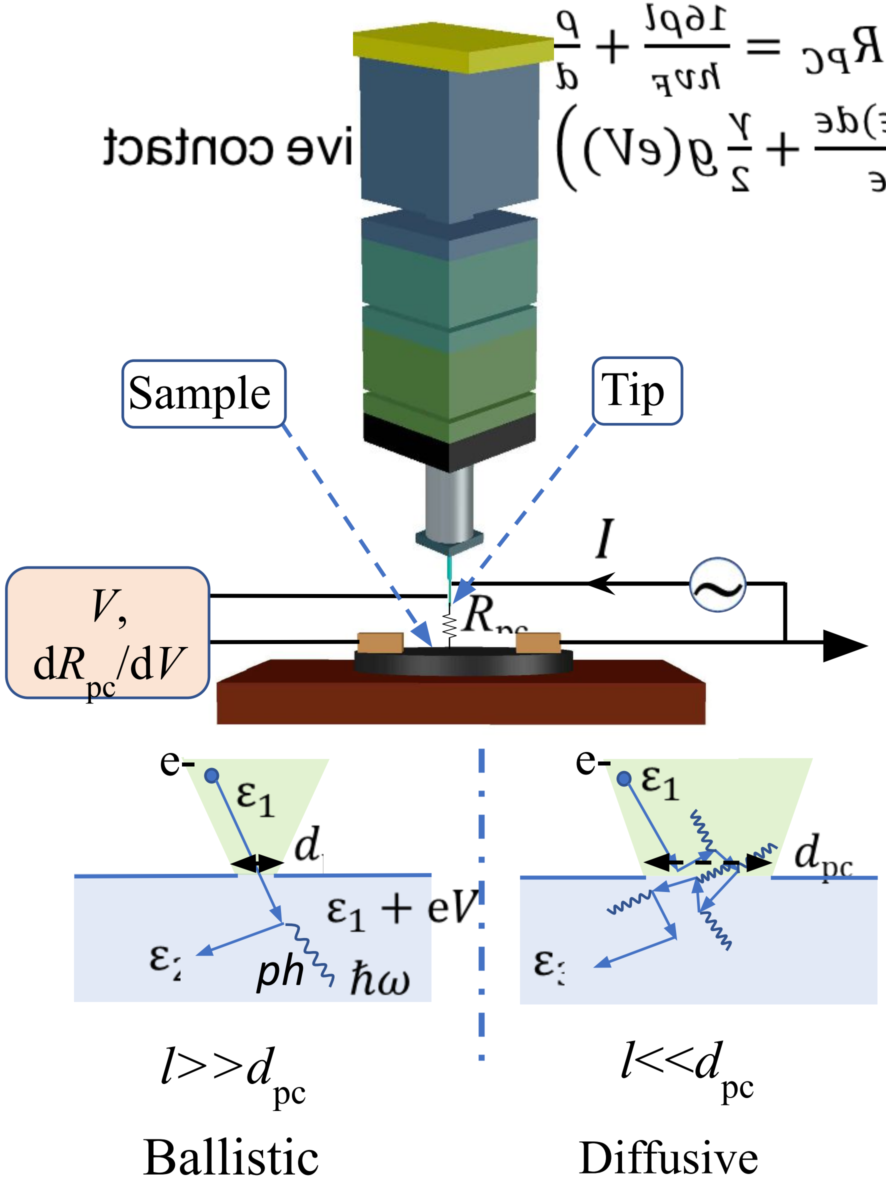
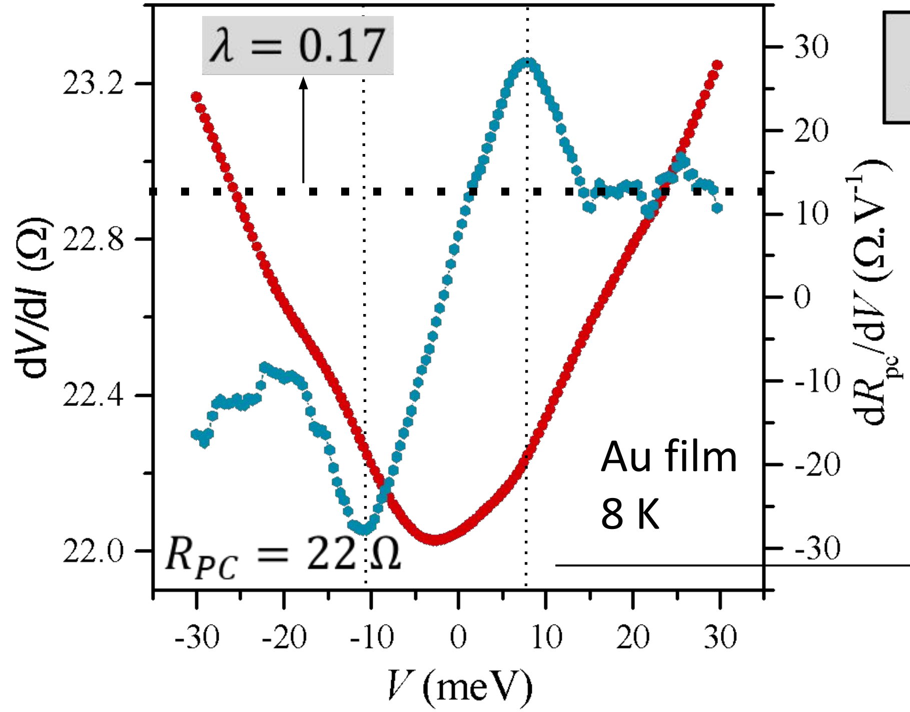
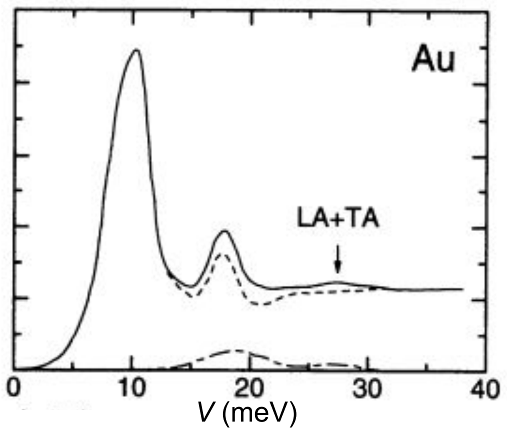




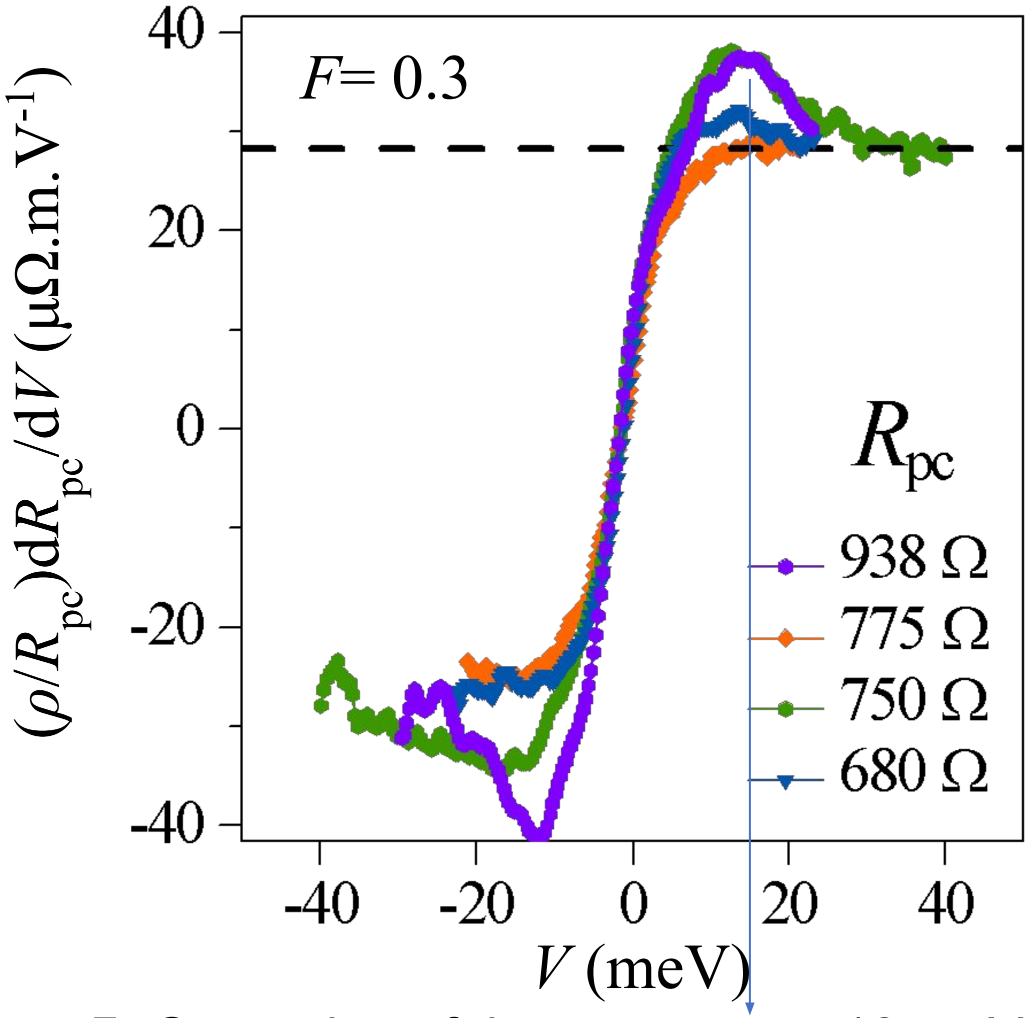
$\lambda = (\text{Const}) \times \frac{dR_{pc}}{dV}(eV \gg \hbar\omega_D)$



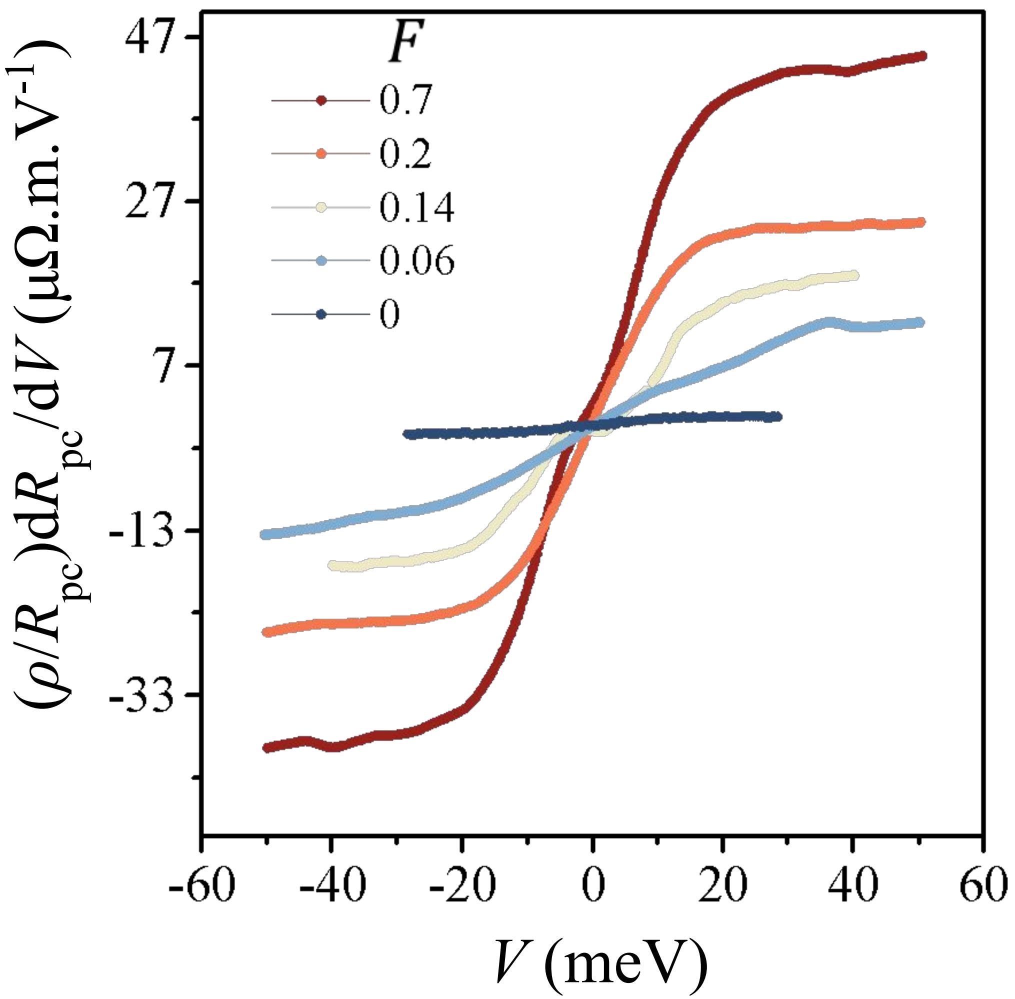
Solid State Commun., 43, 765, 1982

Point contact spectroscopy of nanohybrid films

$$\lambda = \frac{3\pi neh}{16m} d_{pc} \times \frac{dR_{pc}}{dV} (eV \gg h\omega_D)$$

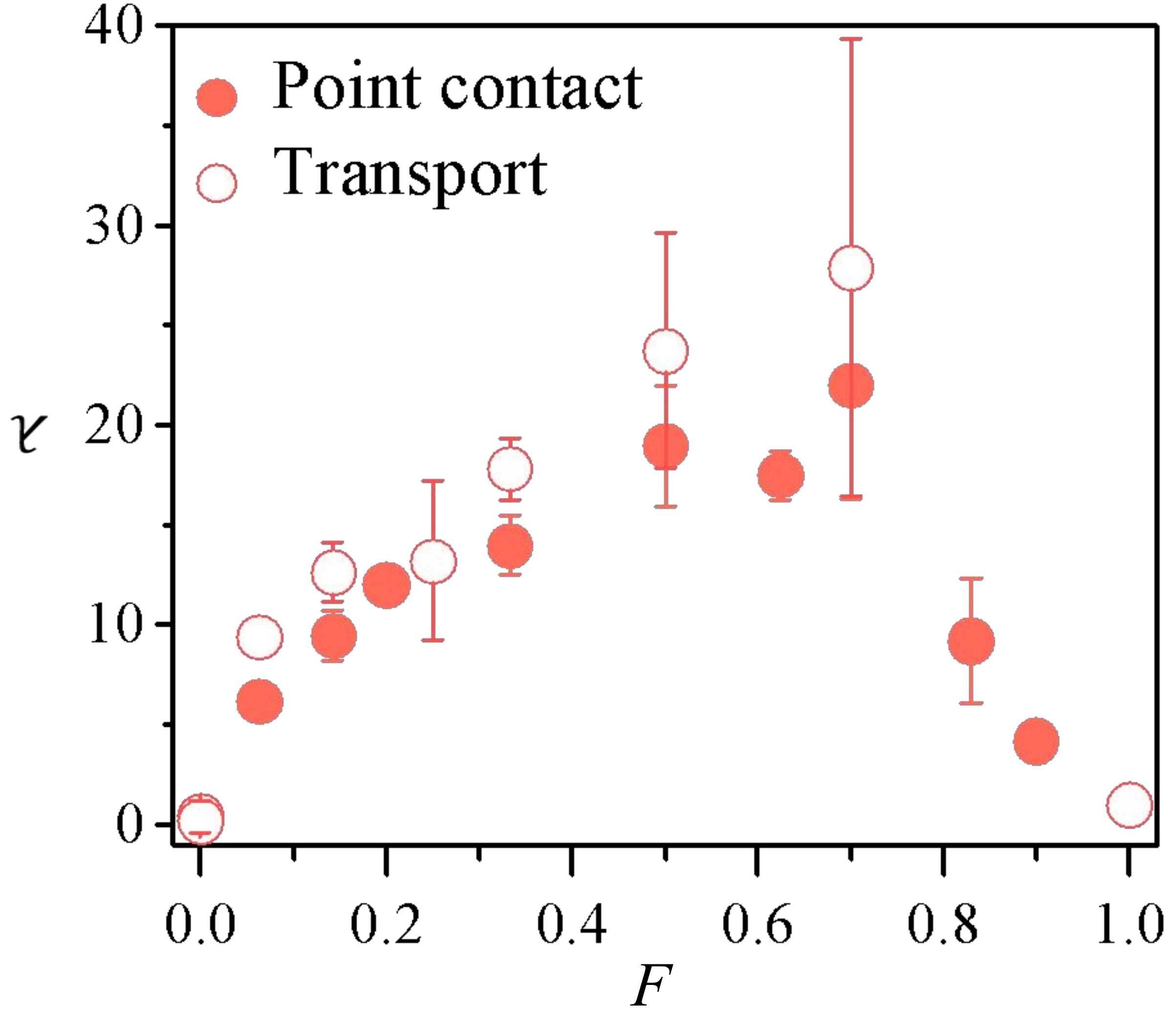


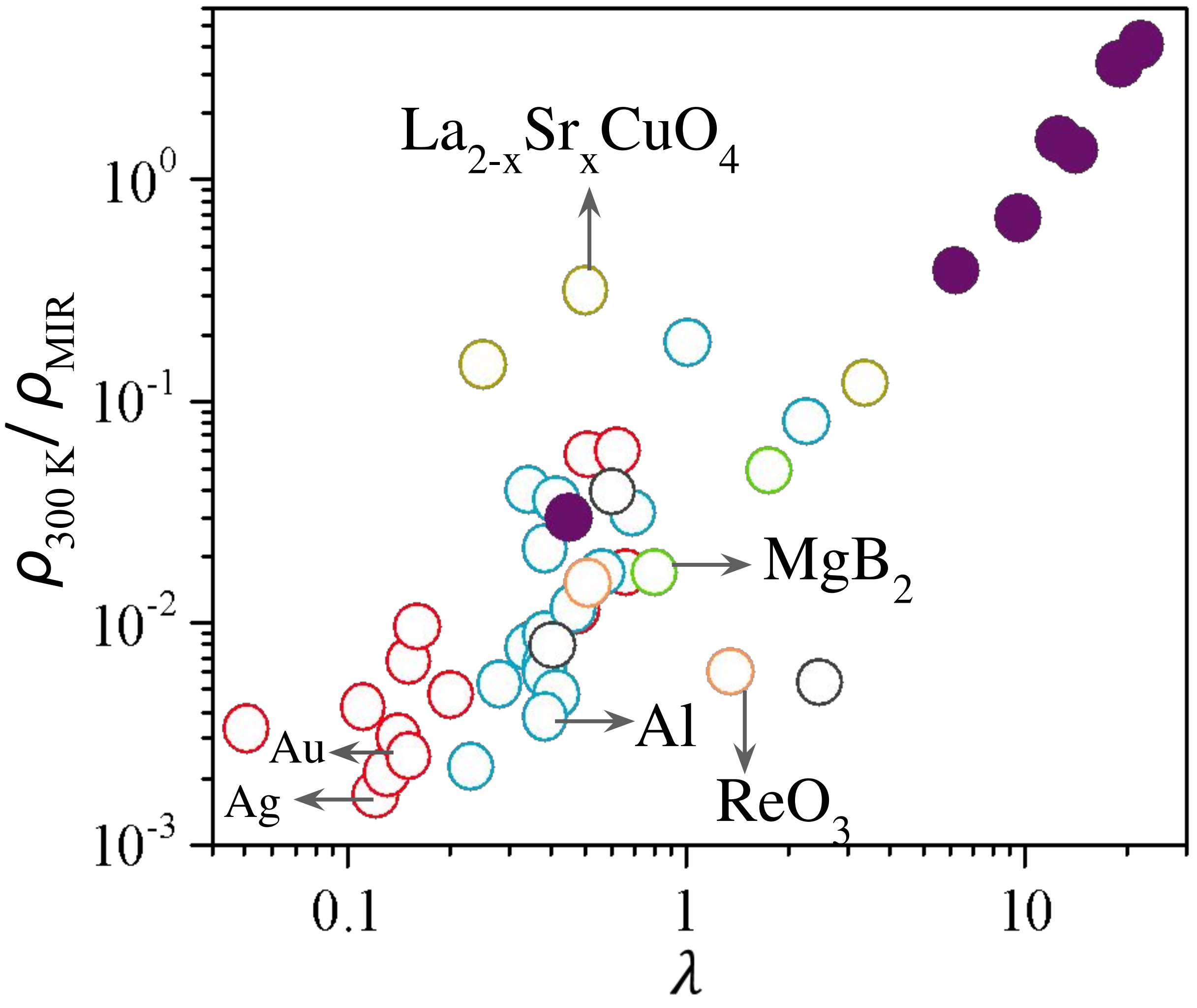
- Saturation of the spectra at ~18 meV
  Acoustic phonons of Au



- Increasing background with *F*

Electron-phonon coupling in metallic nanohybrid films



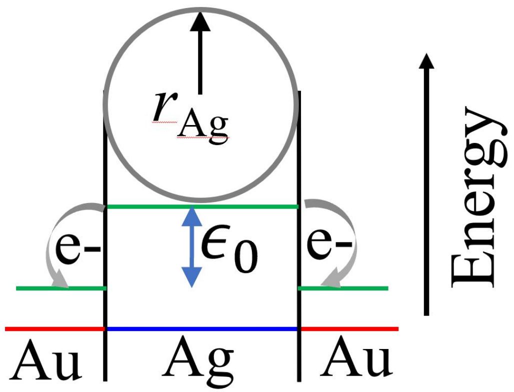


- Significant increase in with *F*

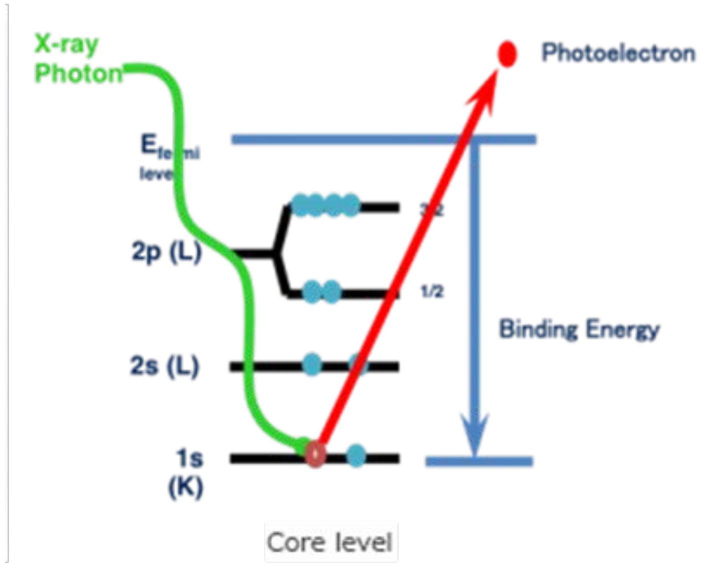
➤ **Universality: $\rho_{300} \propto \lambda$,** Electron-phonon coupling dominates high T resistivity in a wide class of materials

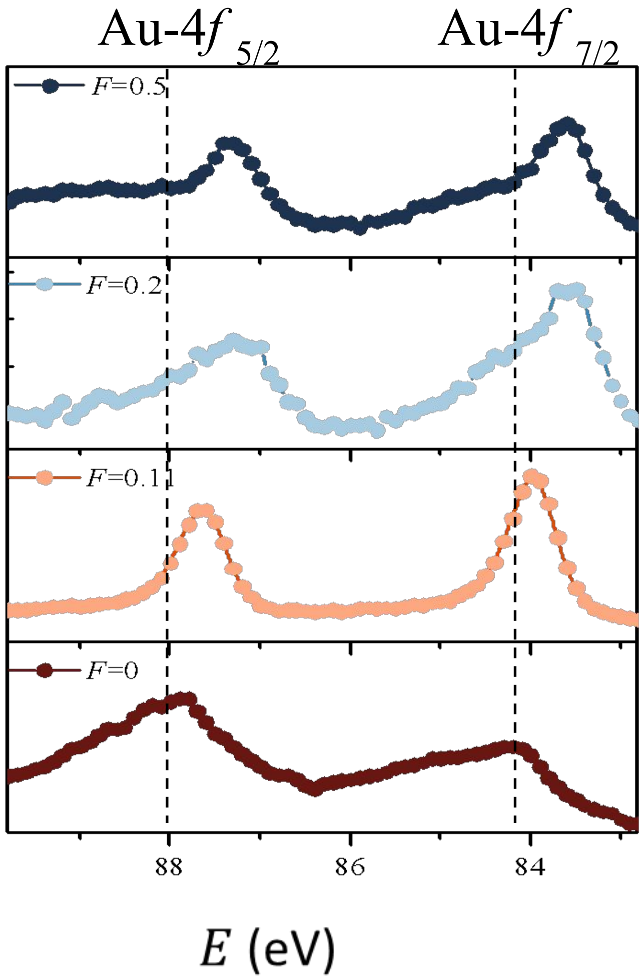
- arXiv:2405.14684v1

Role of nanoscale interfaces

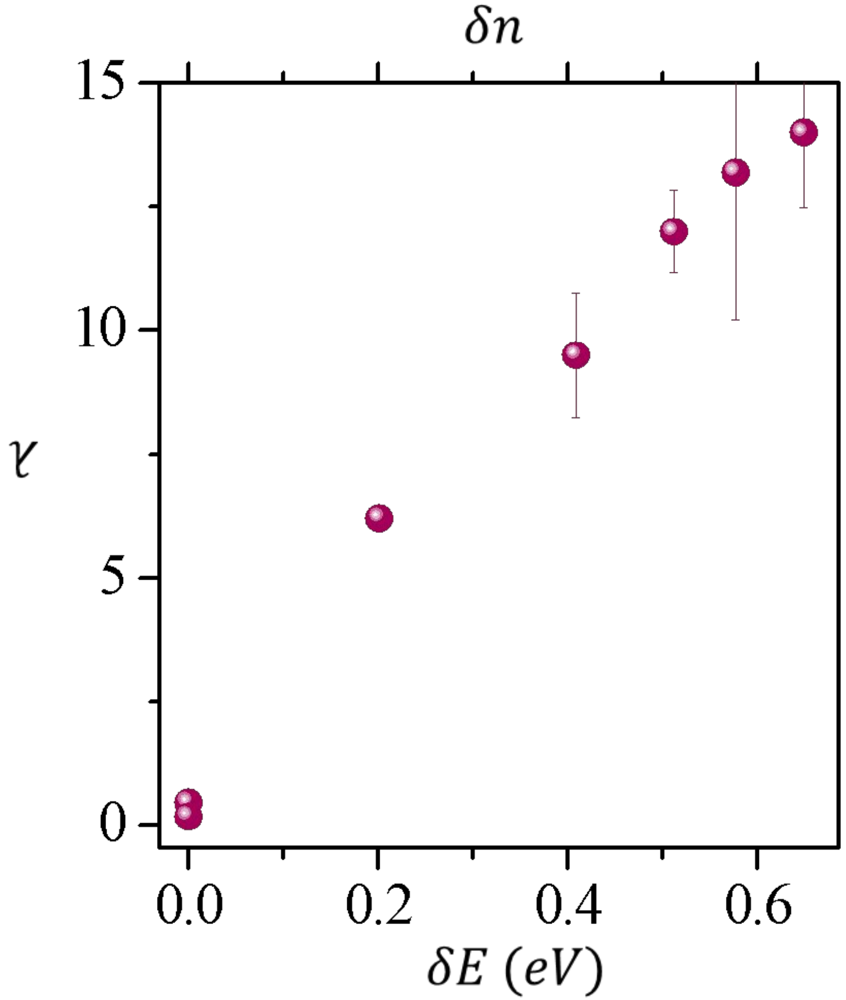


Charge doping from difference in onsite potential





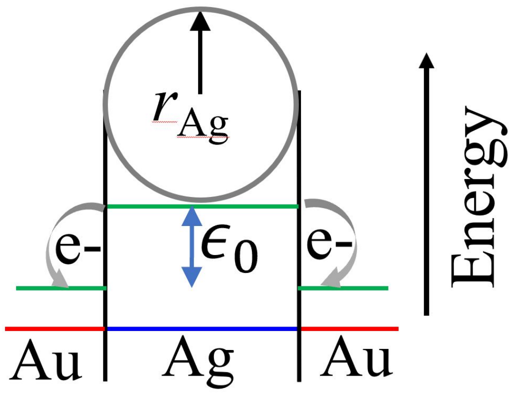
Shift in Au 4f peak in XPS
Charge doping



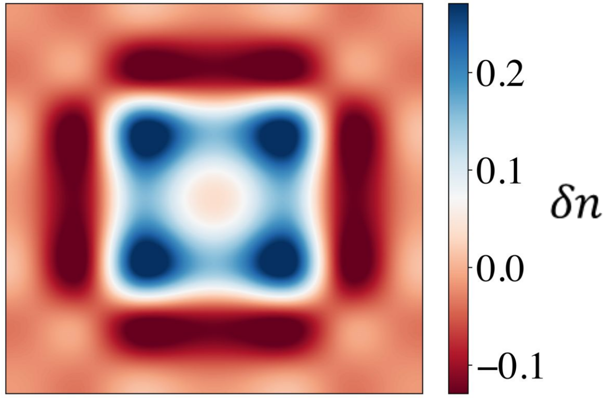
Variation of EPC with interfacial charge transfer

- **Possible role of Coulomb interactions**

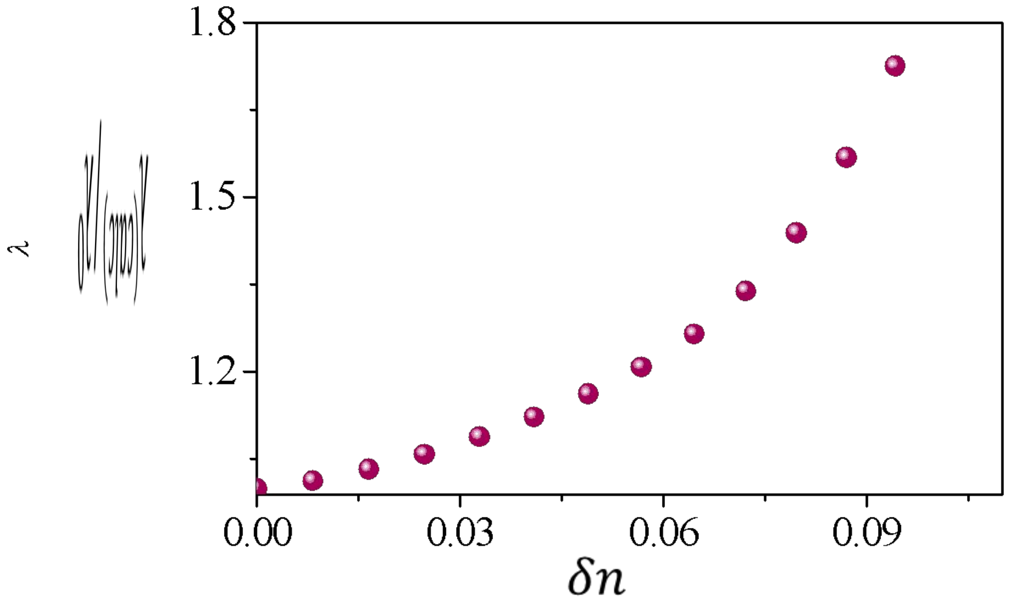
Role of nanoscale interfaces: Theoretical insight



Charge doping from difference in onsite potential



Charge distribution in a square lattice: 4×4 Ag sites surrounded by 8×8 Au sites



- Contributions to the electron-phonon matrix elements from Coulomb interactions of electrons to interfacial charge

$$g_{ce} \propto V_0(\delta n)$$

V_0: Inter-site Coulomb repulsion

- arXiv:2405.14684v1
- Details coming out in another paper soon

Shinjan Mandal

Manish Jain

H R Krishnamurthy

IISc, Bangalore
ICTS, Bangalore

Summary

- Bottom-up metal-nanocomposite
- Unconventional metallic transport: Bad metals
- Buried interfaces of Ag and Au significantly enhance the electron-phonon coupling in noble metals, which have intrinsically the weakest coupling

Questions?

- Origin of high values of EPC
- Existence of metallic state in strong EPC regime
- No crossover to Anderson insulator even for strong disorder
- Possible coexistence of localized and itinerant electrons?

Stay tuned for ***Arindam's talk on 26th July*** *for more details and results!*

Thank you for your attention

EXTRA SLIDES

Scaling of electron-phonon scattering rate

Ignore any non-phonon temperature-dependent scattering

$$\boldsymbol{\rho(T) = \rho_0 + \rho_{e-ph}(T)}$$

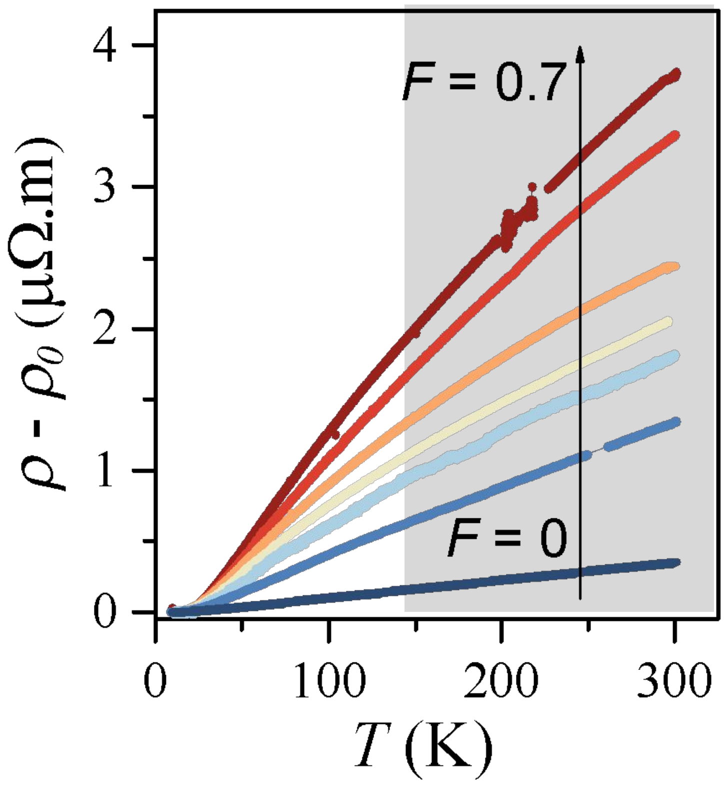
Disorder

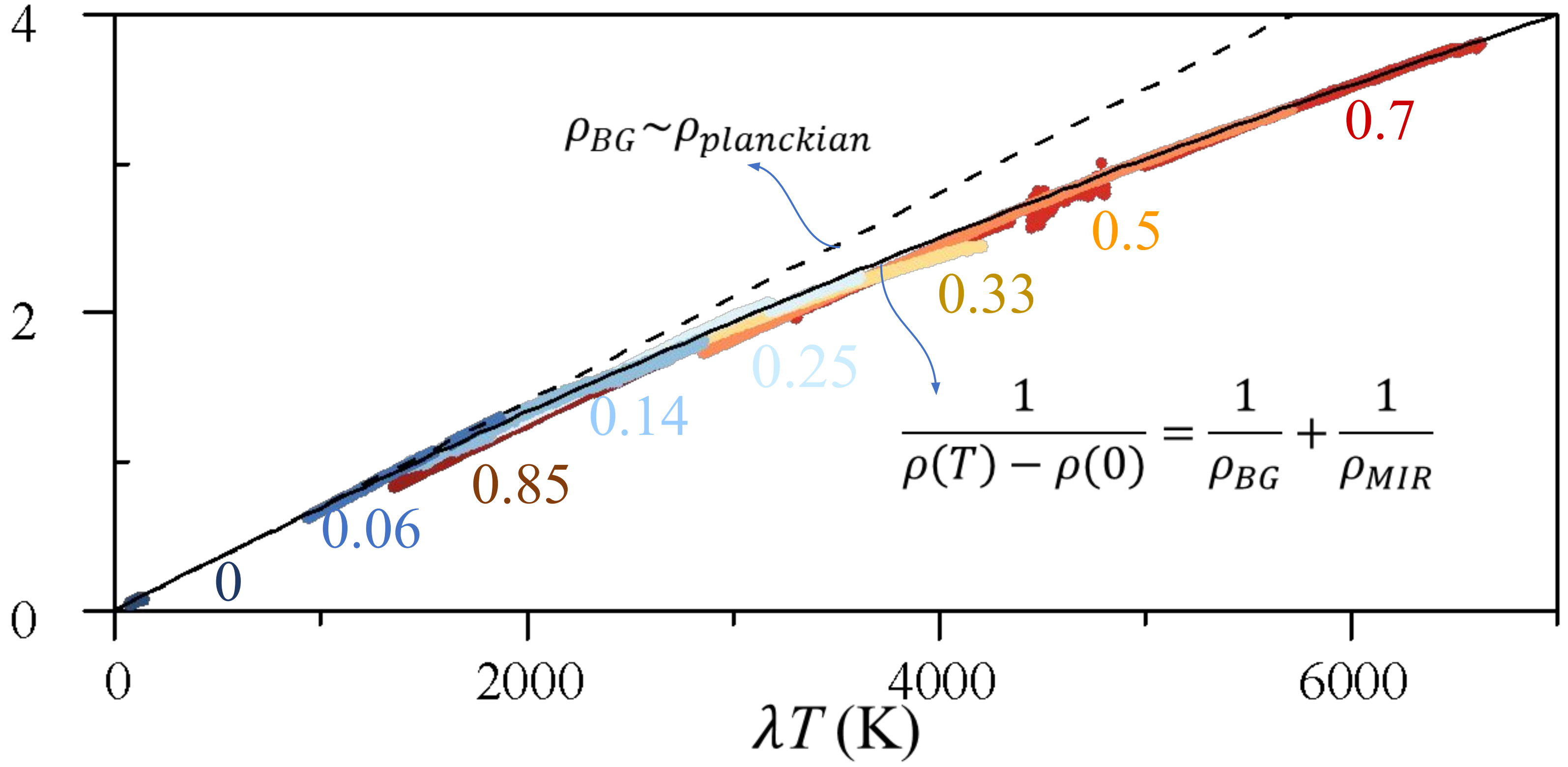
$T > \Theta_D$

$$\rho_{e-ph} = \frac{m}{ne^2\tau_{e-ph}},\ \tau_{e-ph}^{-1}(T) = \left(\frac{2\pi k_B}{\hbar}\right) \times (\lambda T)$$

Planckian bound

Point contact

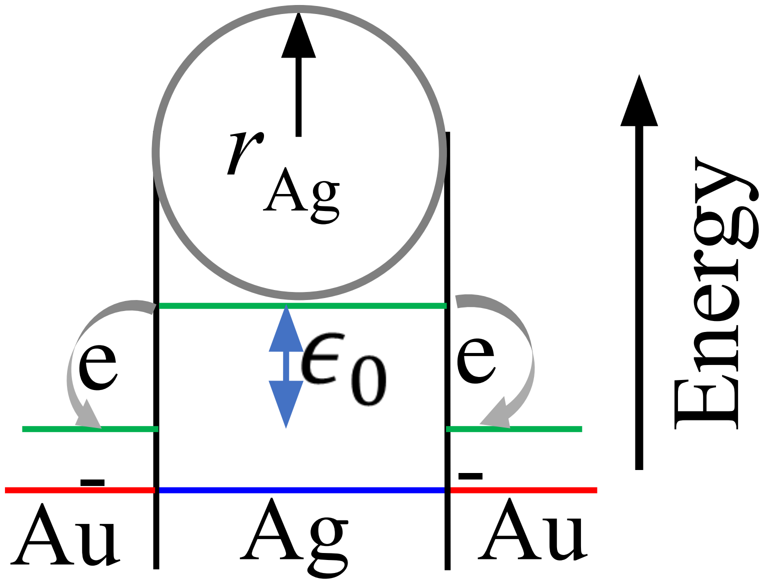


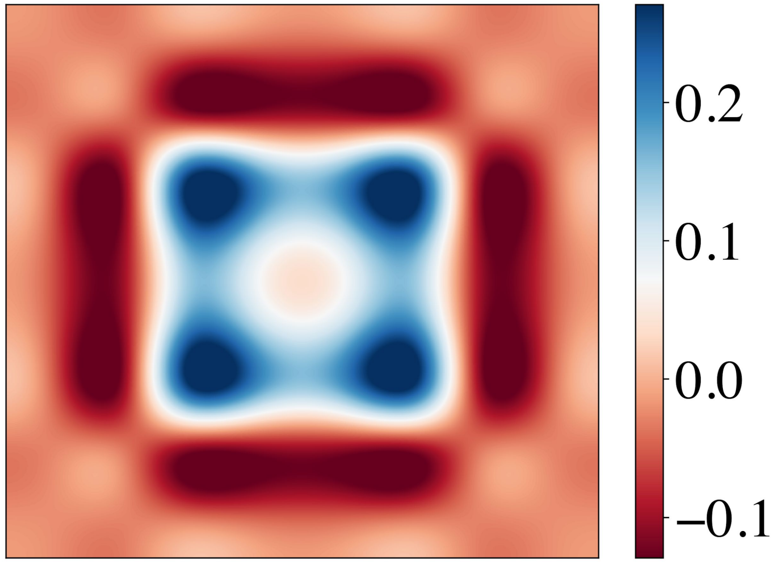


- Bound in scattering rate at ultra-high coupling regimes
- Universality of a two-channel transport

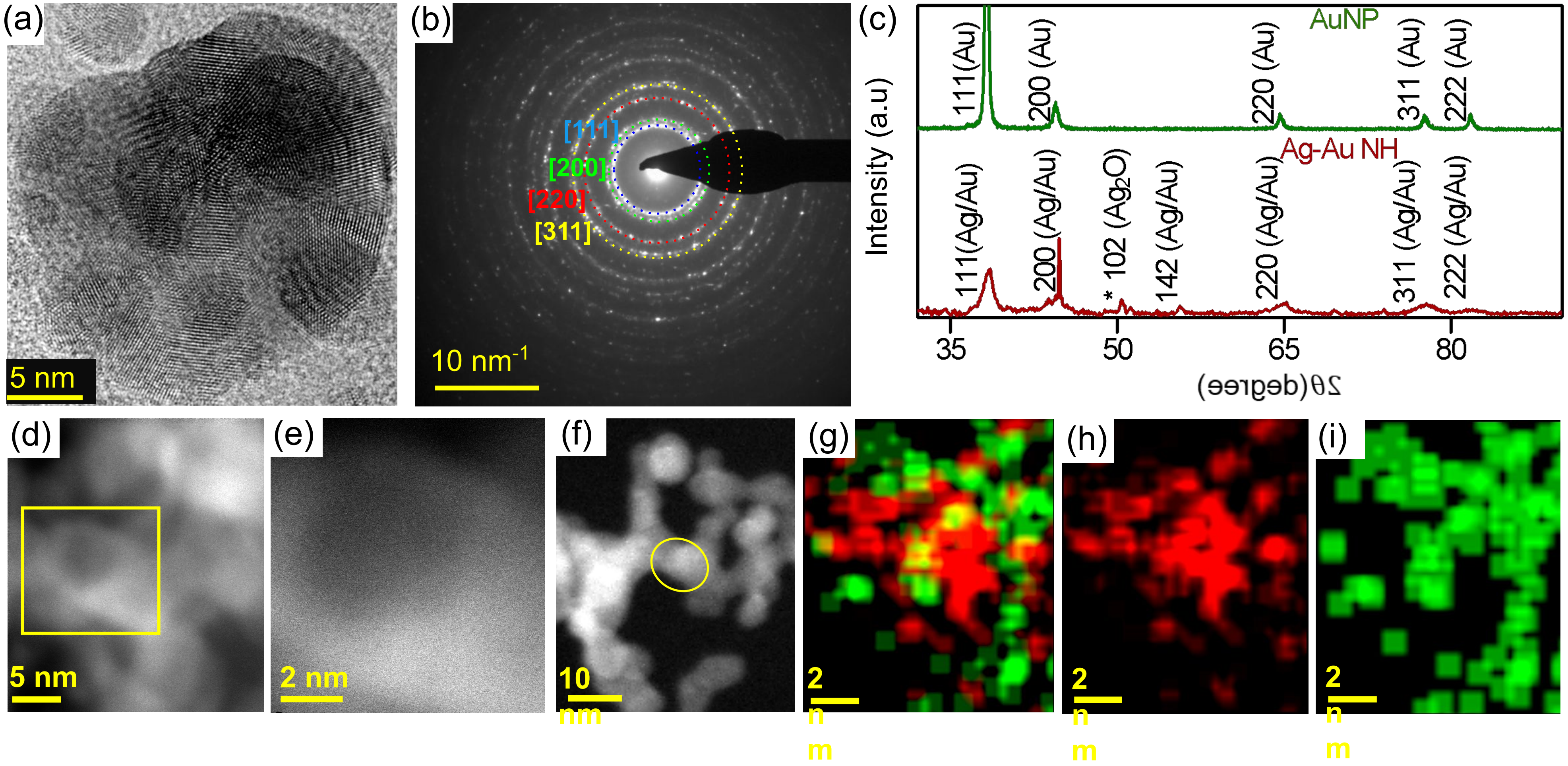
SK, *TK Maji, .. A. Ghosh (arXiv:2405.14684v1)*

Role of nanoscale interfaces





Structure



(a)
5 nm
(b)
[111]
[200]
[220]
[311]
10 nm-1
(c)
AuNP
111(Au)
200 (Au)
220 (Au)
311 (Au)
222 (Au)
Ag-Au NH
111(Ag/Au)
200 (Ag/Au)
* 102 (Ag2O)
142 (Ag/Au)
220 (Ag/Au)
311 (Ag/Au)
222 (Ag/Au)
Intensity (a.u)
35
50
65
80
2θ(degree)
(d)
5 nm
(e)
2 nm
(f)
10 nm
(g)
2 nm
(h)
2 nm
(i)
2 nm

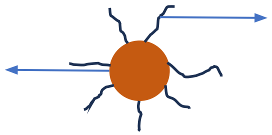
Motivation

Not achieved: Bottom-up assembly of ‘Metal’ with nanoparticles

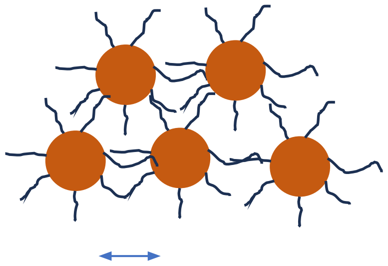
<u>Electron tunneling effects</u>: Coulomb blockade, Variable Range hopping, Activated transport

Surface Capping Agents-Ligands

Nanoparticle



Assembly of nanoparticles



Tunelling gap

Motivation

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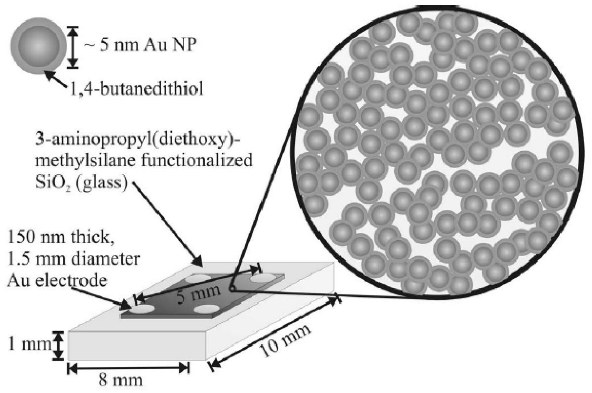
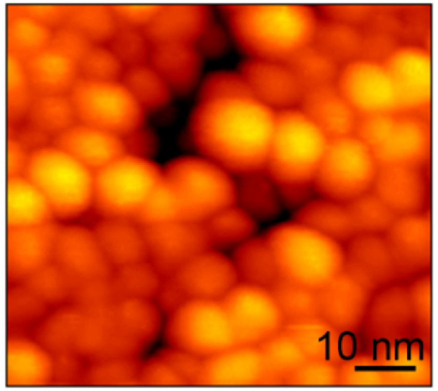
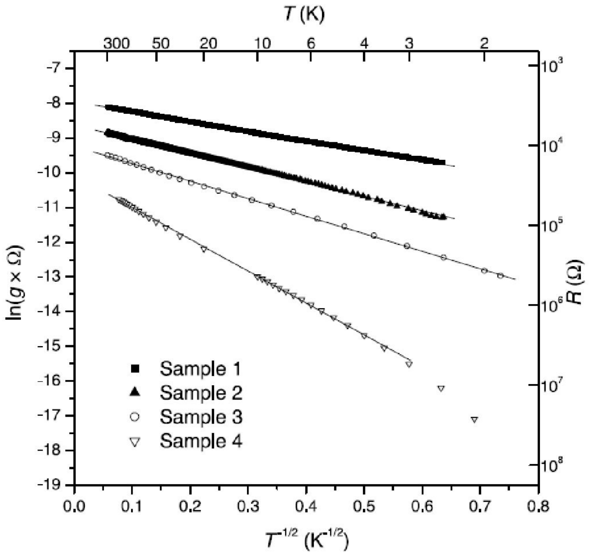
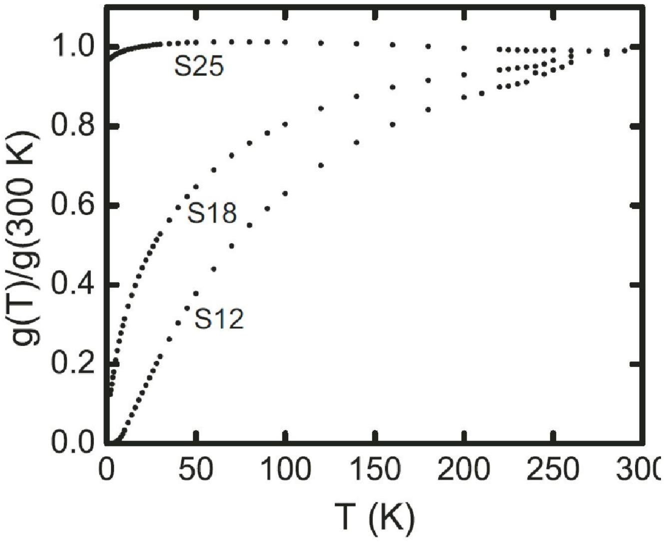
Electron tunneling effects: Coulomb blockade, Variable Range hopping, Activated transport







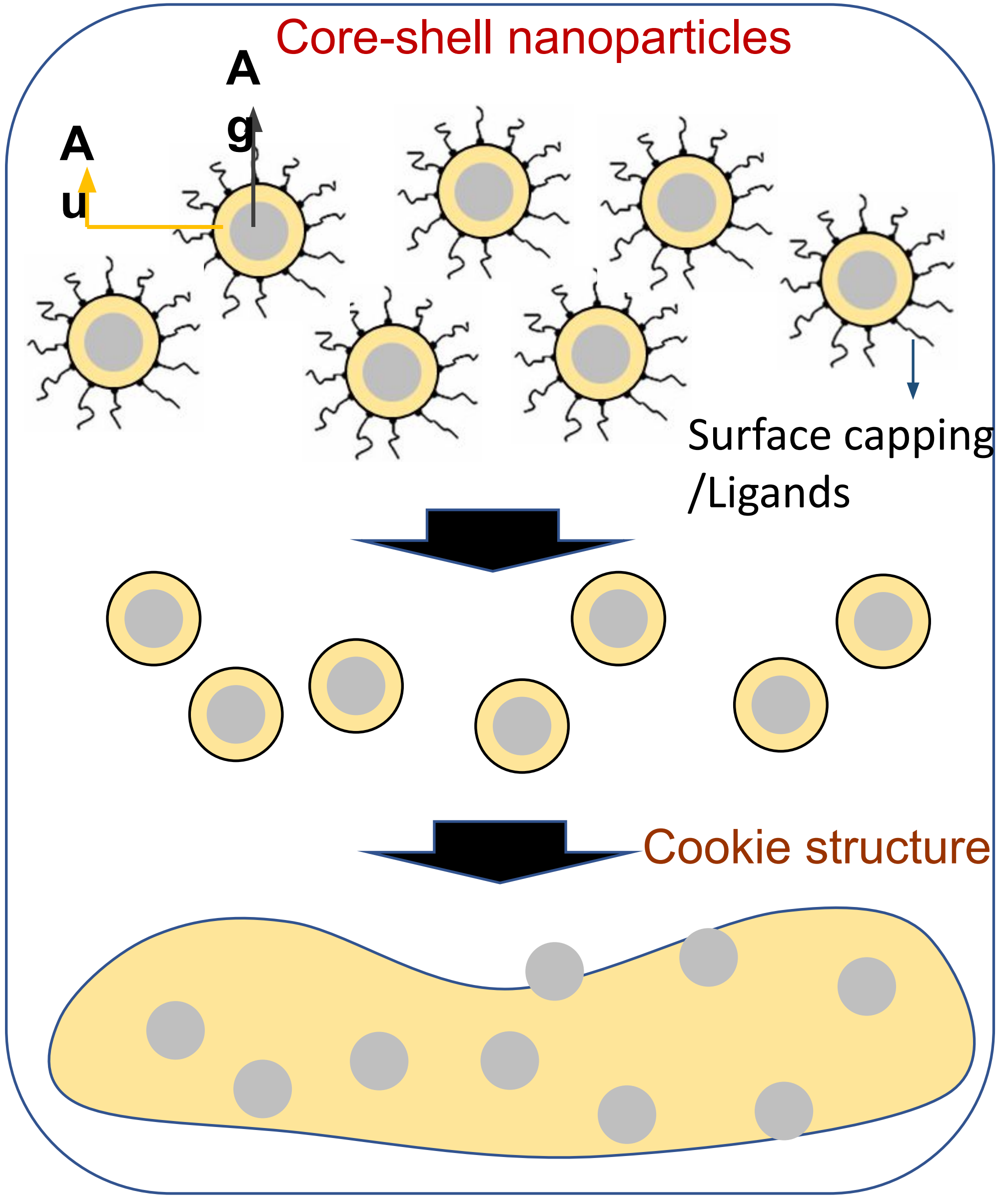


Dunford et al. PRB 74, 115417 (2006)

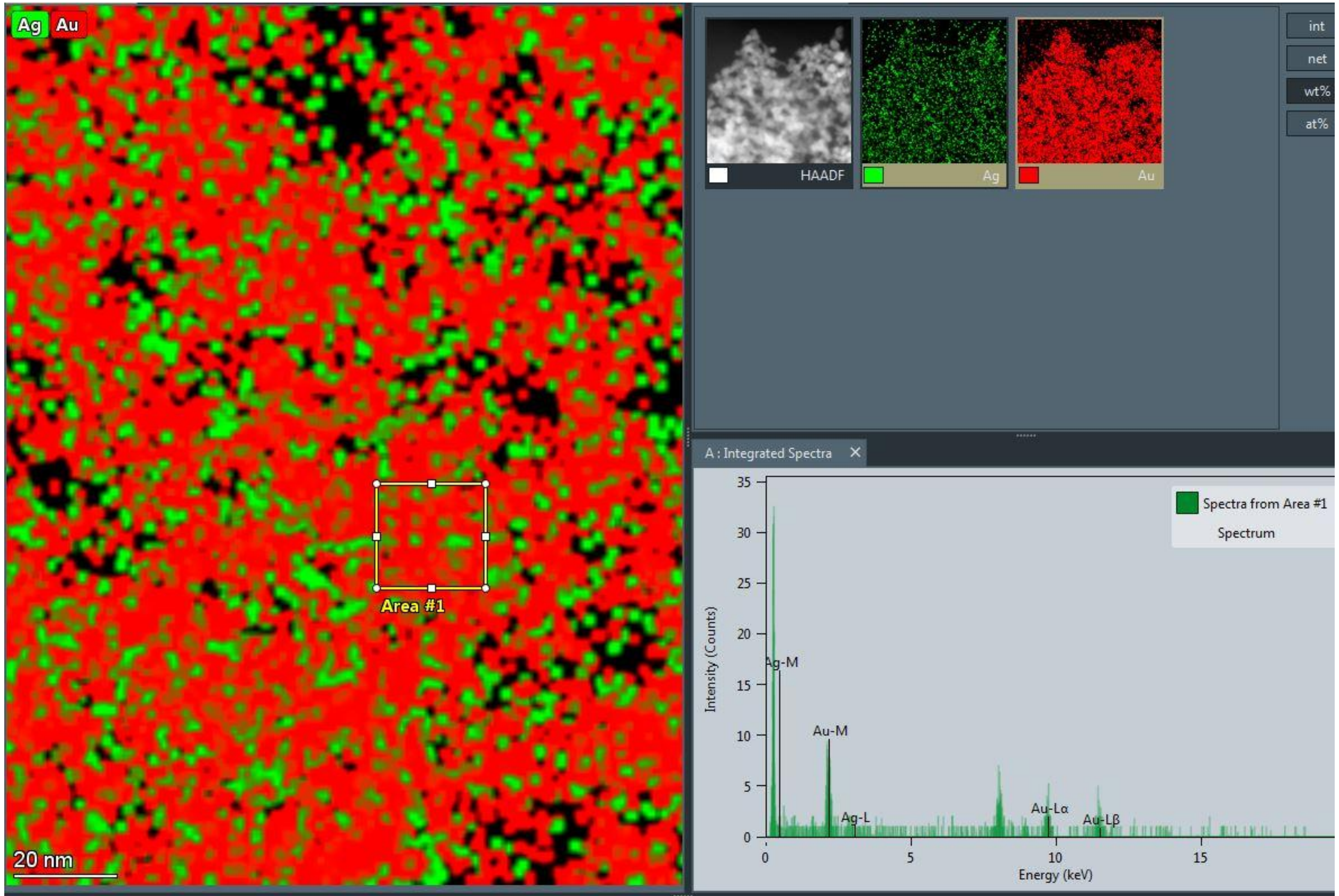
Tran et al. PRB 78, 075437 (2008)

Tie et al. PRB 89, 155117 (2014)

A bi-metallic nano-hybrid



Structure

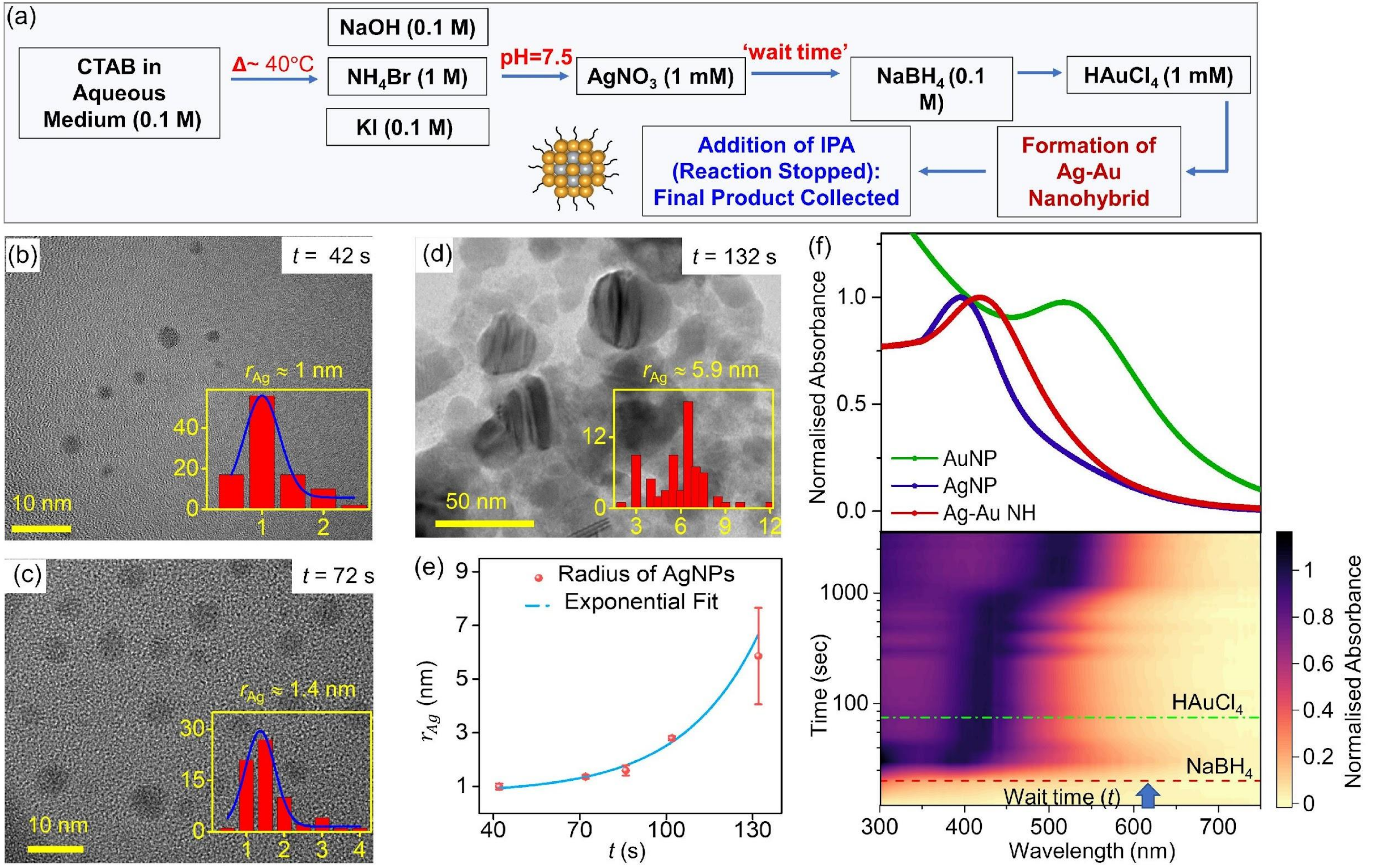


Experiment log

47	Ag	L	19.32	5.62	11.59	2.82	21.21
79	Au	L	80.68	18.81	88.41	15.08	6.16

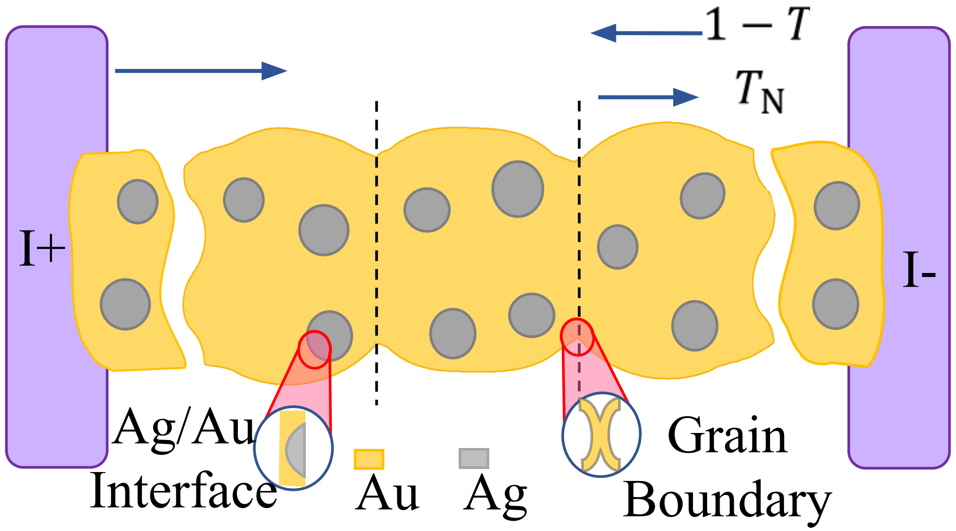
2023-08-12 09:10:16 Analysis of spectrum: Spectra from Area #1

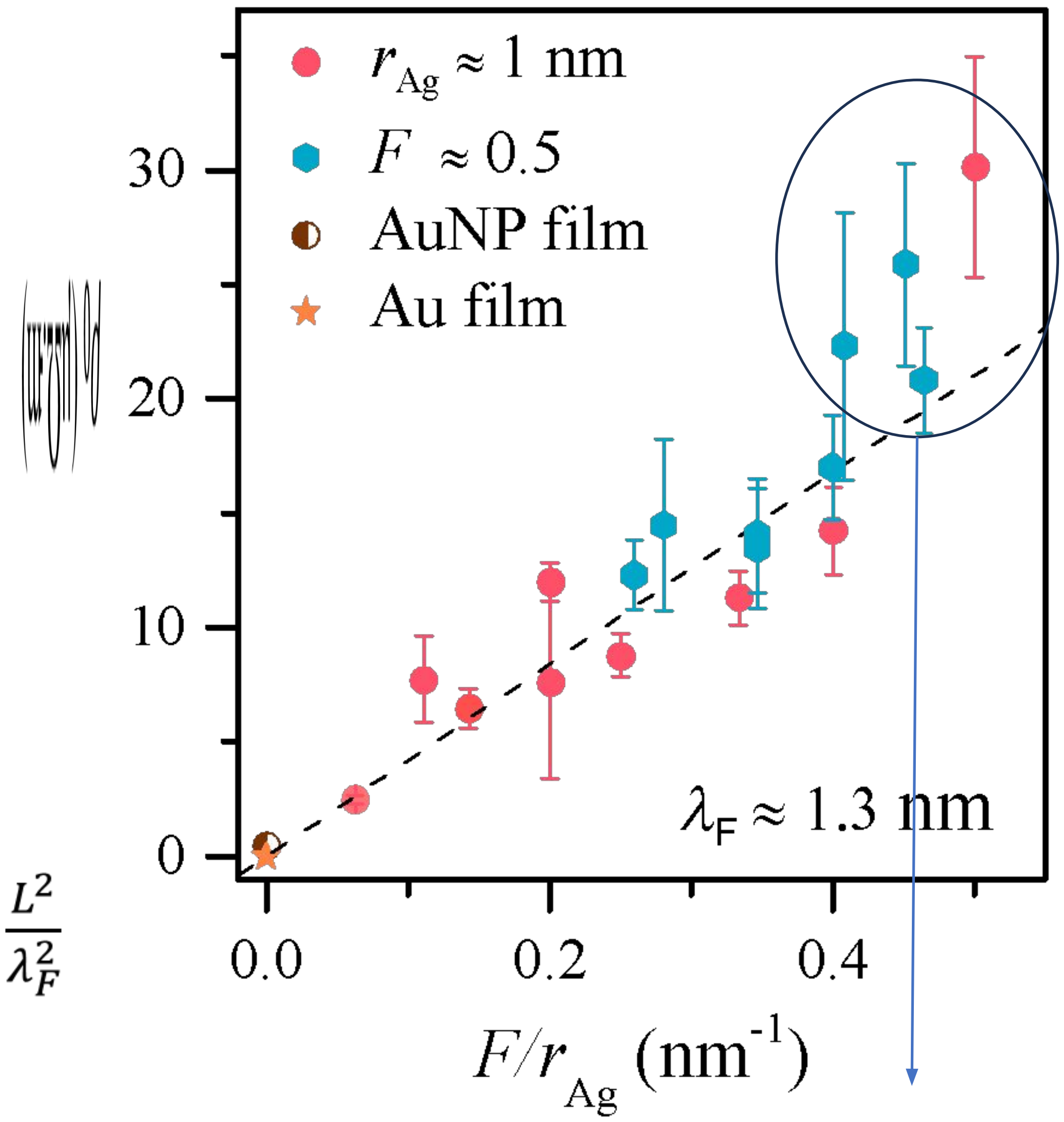
Z	Element	Family	Atomic Fraction (%)	Atomic Error (%)	Mass Fraction (%)	Mass Error (%)	Fit error (%)
47	Ag	L	21.73	5.80	13.19	2.87	18.22
79	Au	L	78.27	17.90	86.81	14.63	6.05



(a)
CTAB in Aqueous Medium (0.1 M)
Δ~ 40°C
NaOH (0.1 M)
NH_4Br (1 M)
KI (0.1 M)
pH=7.5
$AgNO_3$ (1 mM)
'wait time'
$NaBH_4$ (0.1 M)
$HAuCl_4$ (1 mM)
Formation of Ag-Au Nanohybrid
Addition of IPA (Reaction Stopped): Final Product Collected
(b)
t = 42 s
r_{Ag} ≈ 1 nm
10 nm
(c)
t = 72 s
r_{Ag} ≈ 1.4 nm
10 nm
(d)
t = 132 s
r_{Ag} ≈ 5.9 nm
50 nm
(e)
Radius of AgNPs
Exponential Fit
r_{Ag} (nm)
t (s)
(f)
Normalised Absorbance
AuNP
AgNP
Ag-Au NH
Time (sec)
$HAuCl_4$
$NaBH_4$
Wait time (t)
Wavelength (nm)
Normalised Absorbance

Resistivity – interface correlation





- <u>Interface of AgNPs as dominant scatterers</u>
- Mean free path : $\lambda = \frac{1}{\sigma n}$
- **Landauer-Buttiker formalism** :

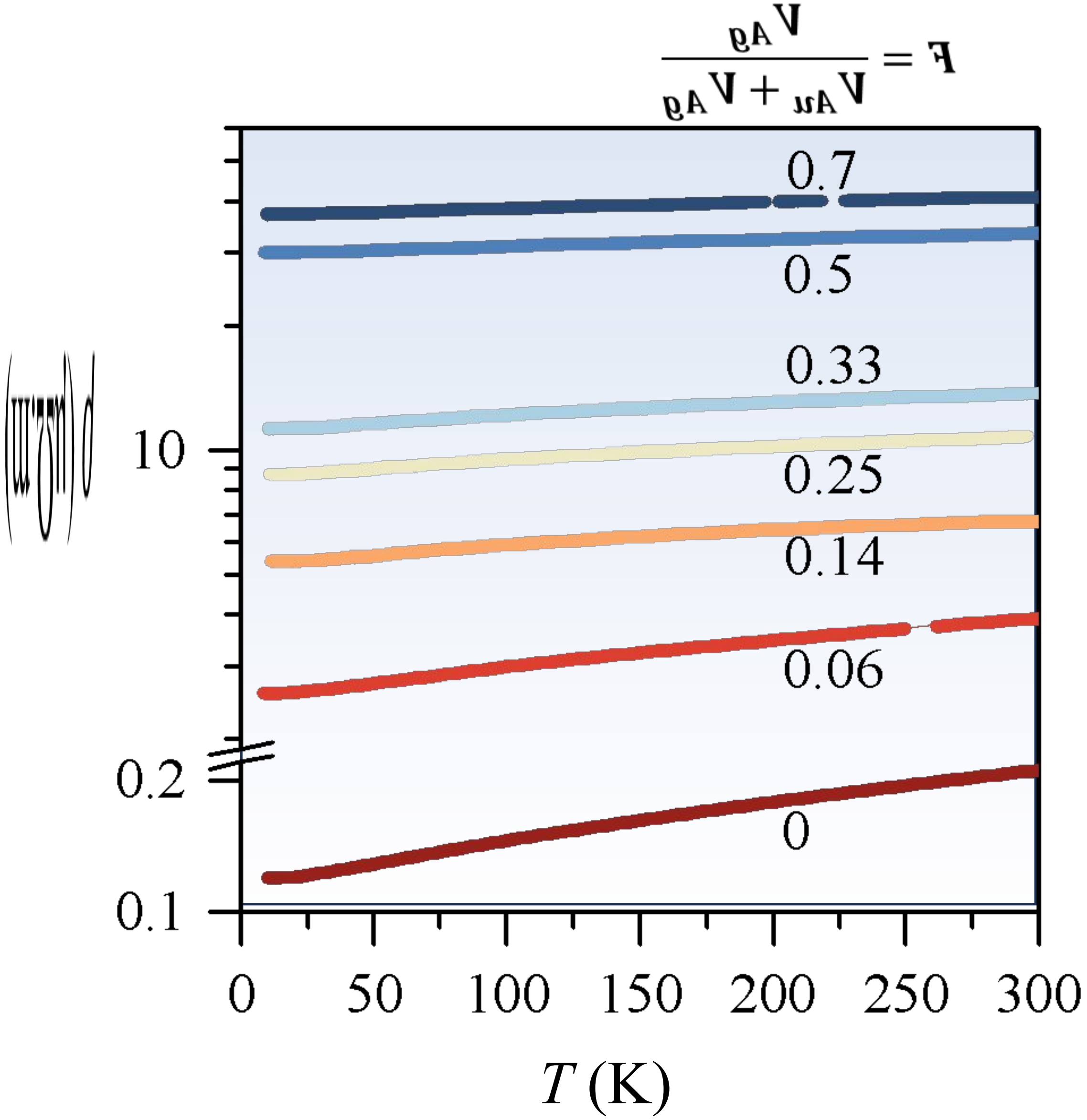
$$R = \frac{h}{e^2}\frac{(1-T_N)}{MT_N},\ T_N = \frac{\lambda}{L+\lambda},\ M : \text{no. of modes} = \frac{L^2}{\lambda_F^2}$$

$$\boldsymbol{\rho_0 = \frac{h}{e^2}\frac{\lambda_F^2}{r_{Ag}}\frac{f}{1+f}}$$

Resistivity approaching the Mott-Ioffe-Regel limit!

Resistivity saturation

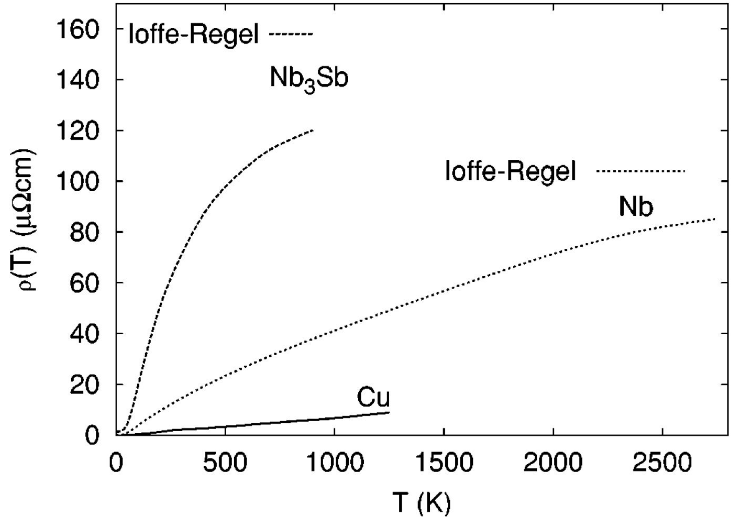
The Mott-Ioffe-Regel (MIR) Limit and ‘bad metals’



MIR Limit: $k_F l = 1$ $\rho_{MIR}^{Au} = 24.6\ \mu\Omega\text{-m}$

$$\rho_{MIR} = \frac{3\pi^2\hbar}{e^2 k_F^2 (k_F l)} = \frac{3\pi^2\hbar}{e^2 k_F}$$

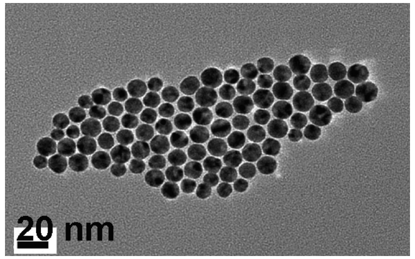
- **Mean-free path approaching inter-atomic distance**
- **Ill-defined quasiparticles**



Gunnarsson, Calandra, Han Rev Mod Phys 2003 75, 1085

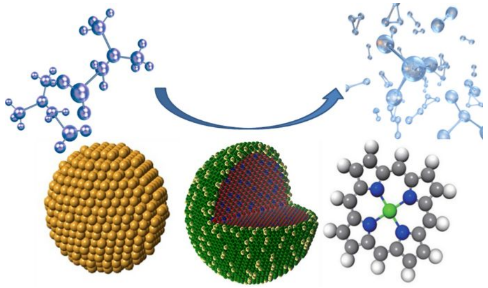
Metal Nanoparticles-A primer:

Nanoparticles
- Metal Nanoparticles $\sim 1 - 100\ nm$



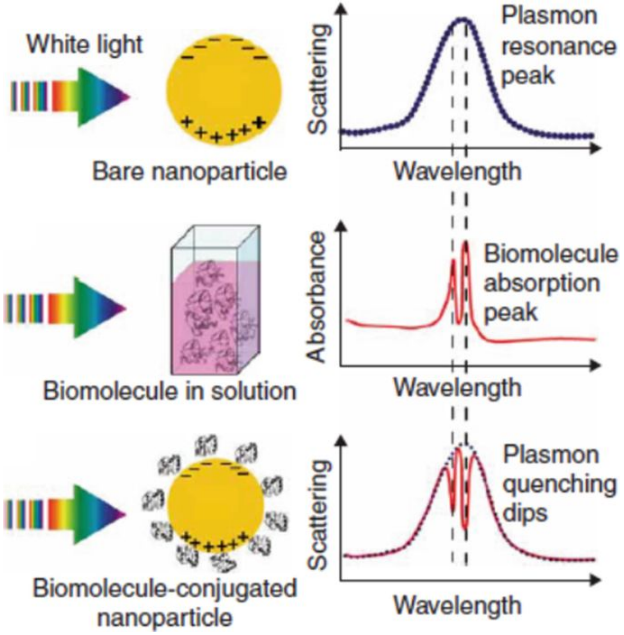
High Surface to volume ratio

- Catalysis
- Drug delivery



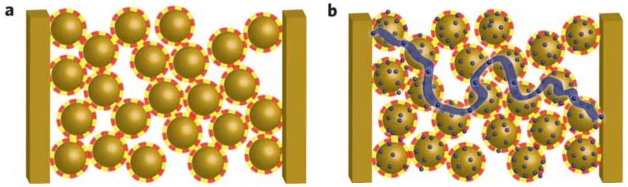
Localized Surface Plasmon Band

- Sensing
- Imaging
- Surface enhanced Raman scattering
- Opto-electronic devices



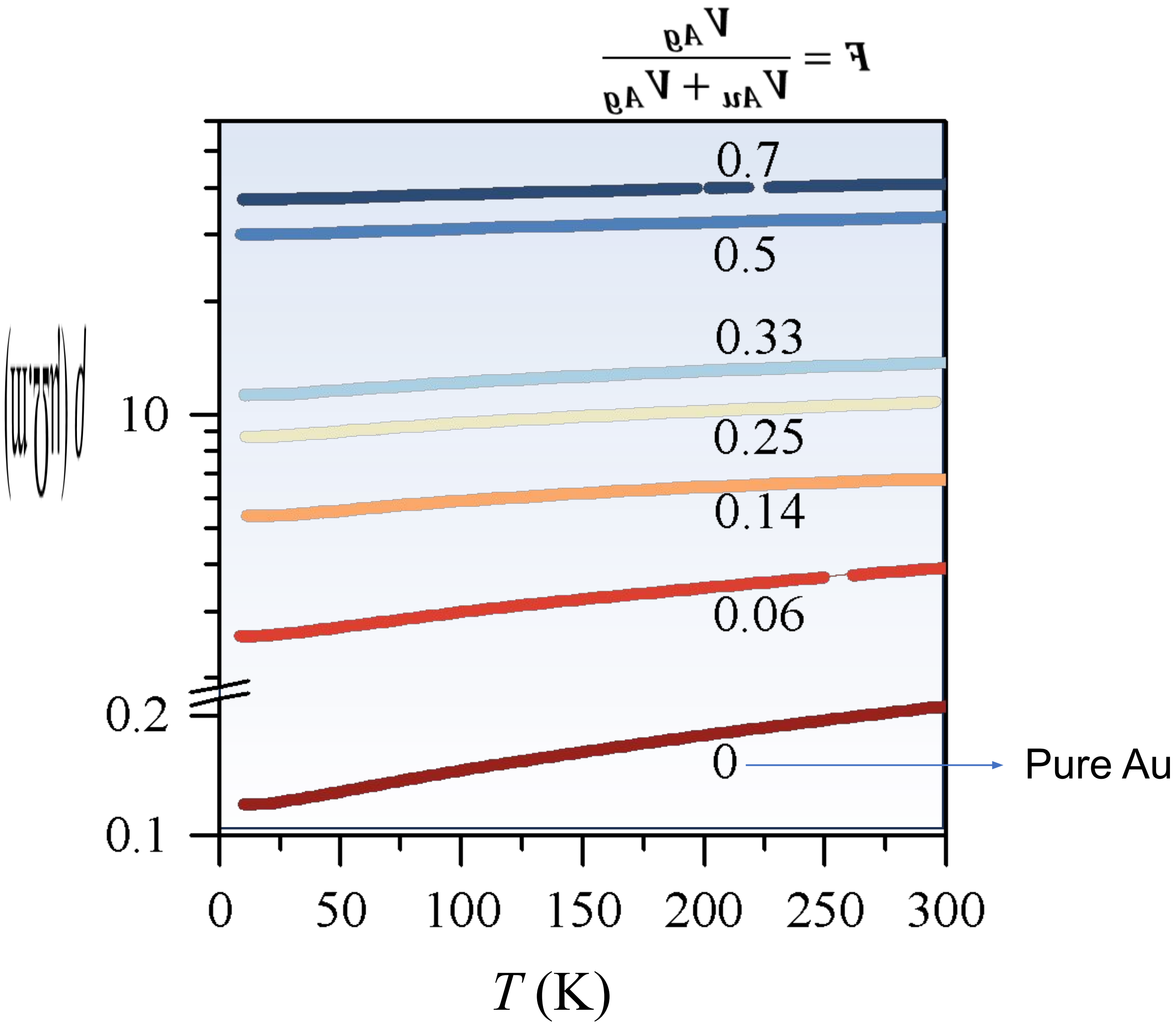
Quantum confinement: **Electron tunneling**

- Sensors
- Memristive Switching
- Chemoelectronics



Change in tunnelling current for sensing applications

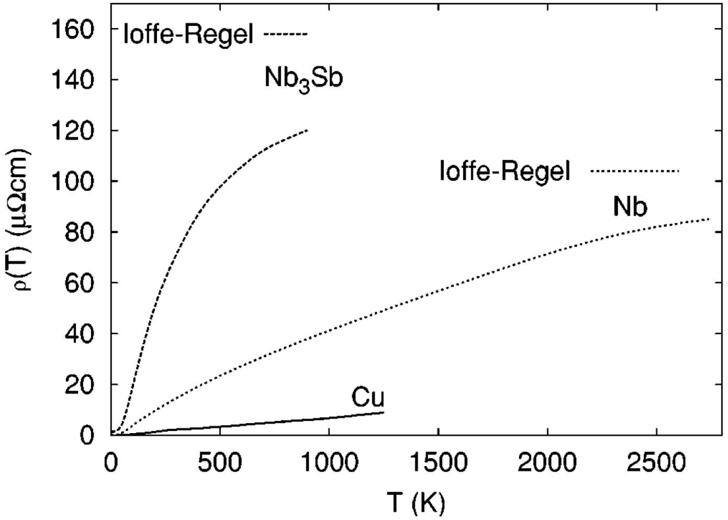
The Mott-Ioffe-Regel (MIR) Limit and ‘bad metals’



MIR Limit: $k_F l = 1$ $\rho_{MIR}^{Au} = 24.6\ \mu\Omega\text{-m}$

$$\rho_{MIR} = \frac{3\pi^2\hbar}{e^2 k_F (k_F l)} = \frac{3\pi^2\hbar}{e^2 k_F}$$

- **Mean-free path approaching inter-atomic distance**
- **Ill-defined quasiparticles**

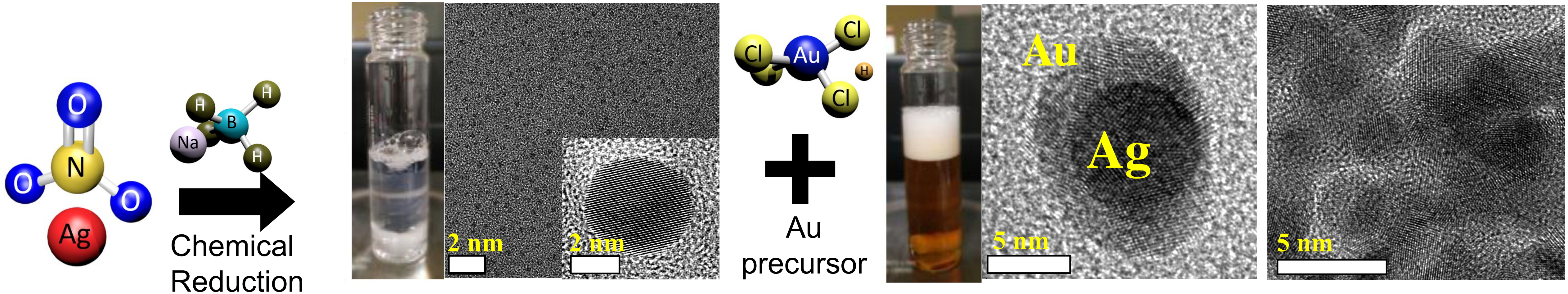


Gunnarsson, Calandra, Han Rev Mod Phys 2003 75, 1085

Chemical route – The process flow

ACS Appl. Electron. Mater. 2023, 5, 5, 2893–2901

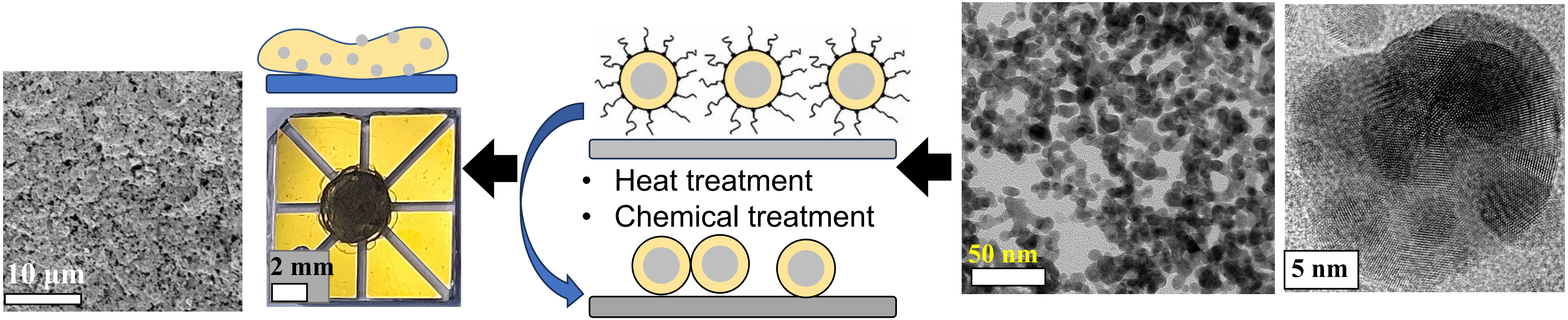
Ag(NP) – Au hybrid



Ag precursor

Ag nanoparticles

Ag@Au nanohybrid



Film for transport measurements

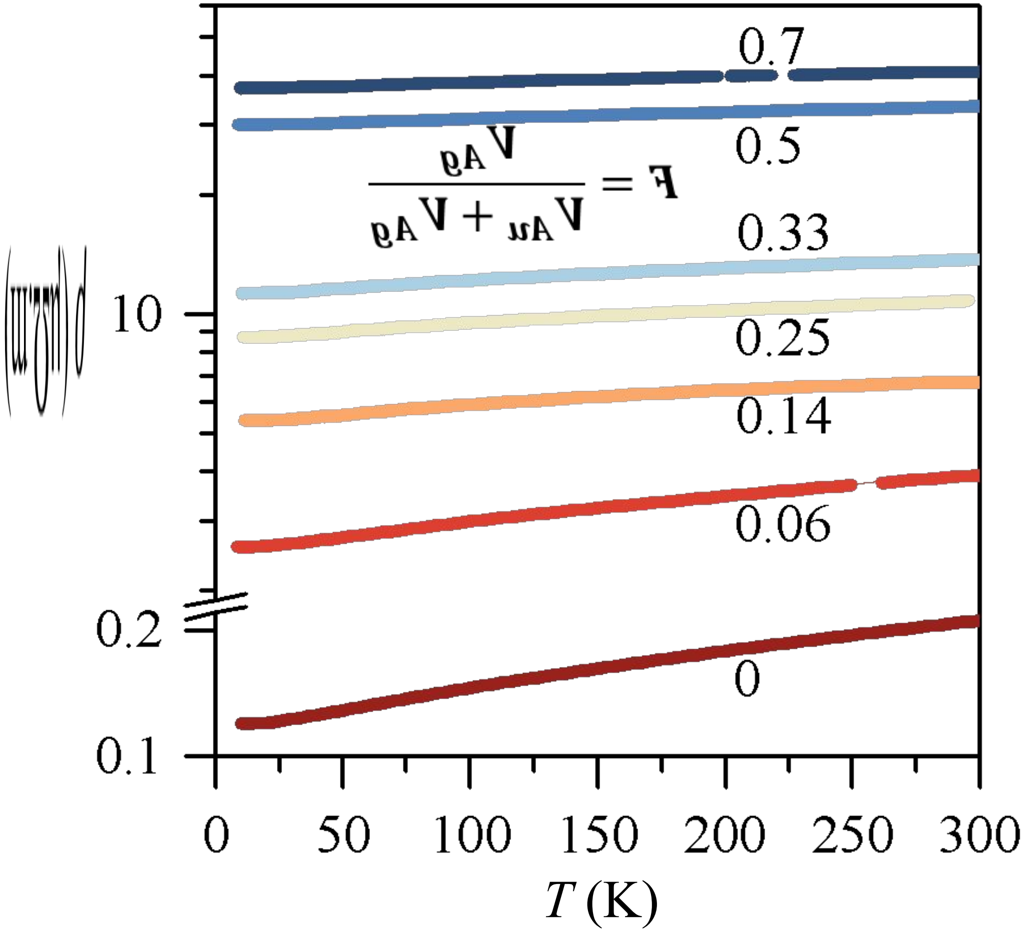
Ligand removal and cross-linking

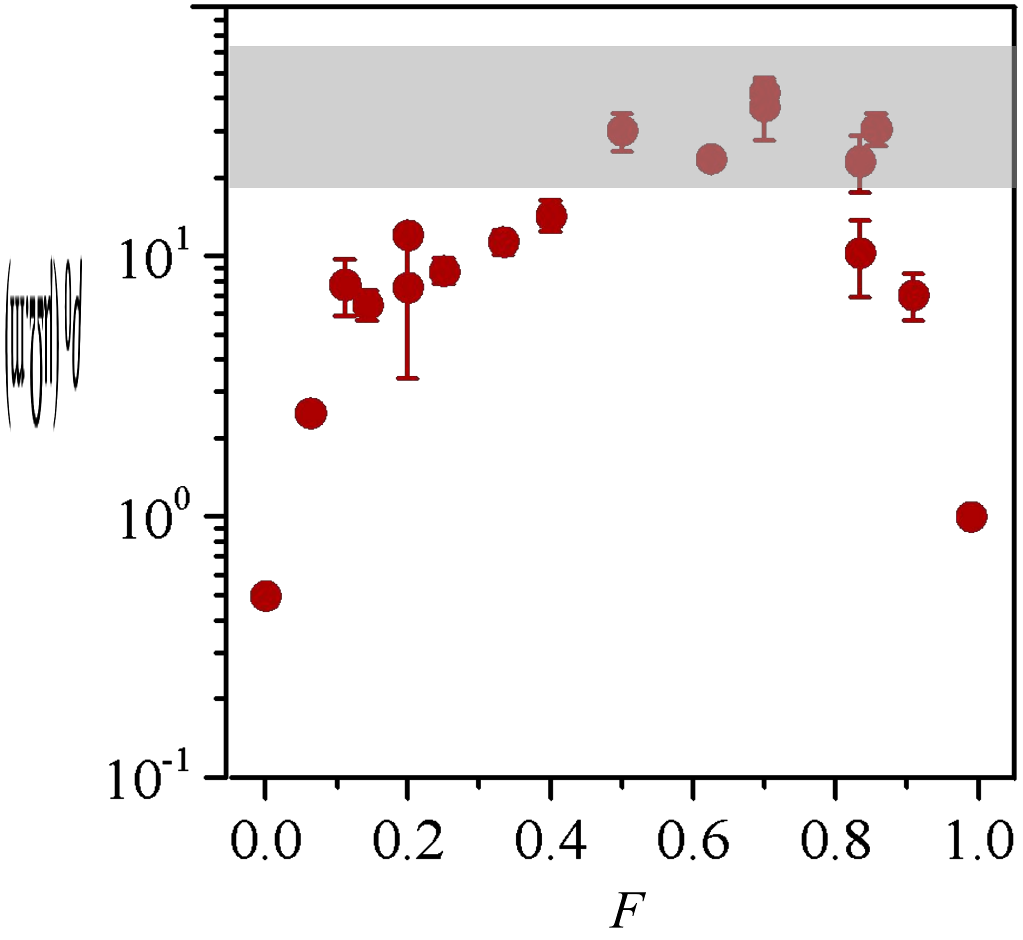
Clustering

Resistivity saturation

The Mott-Ioffe-Regel (MIR) Limit and ‘bad metals’

MIR Limit: $k_F l = 1$ $\rho_{MIR}^{Au} = 24.6\ \mu\Omega\text{-m}$





- Saturation in T-dependent resistivity close to the MIR limit

Bound in the residual resistivity (disorder) in the range F~0.4 – 0.8 towards the MIR limit