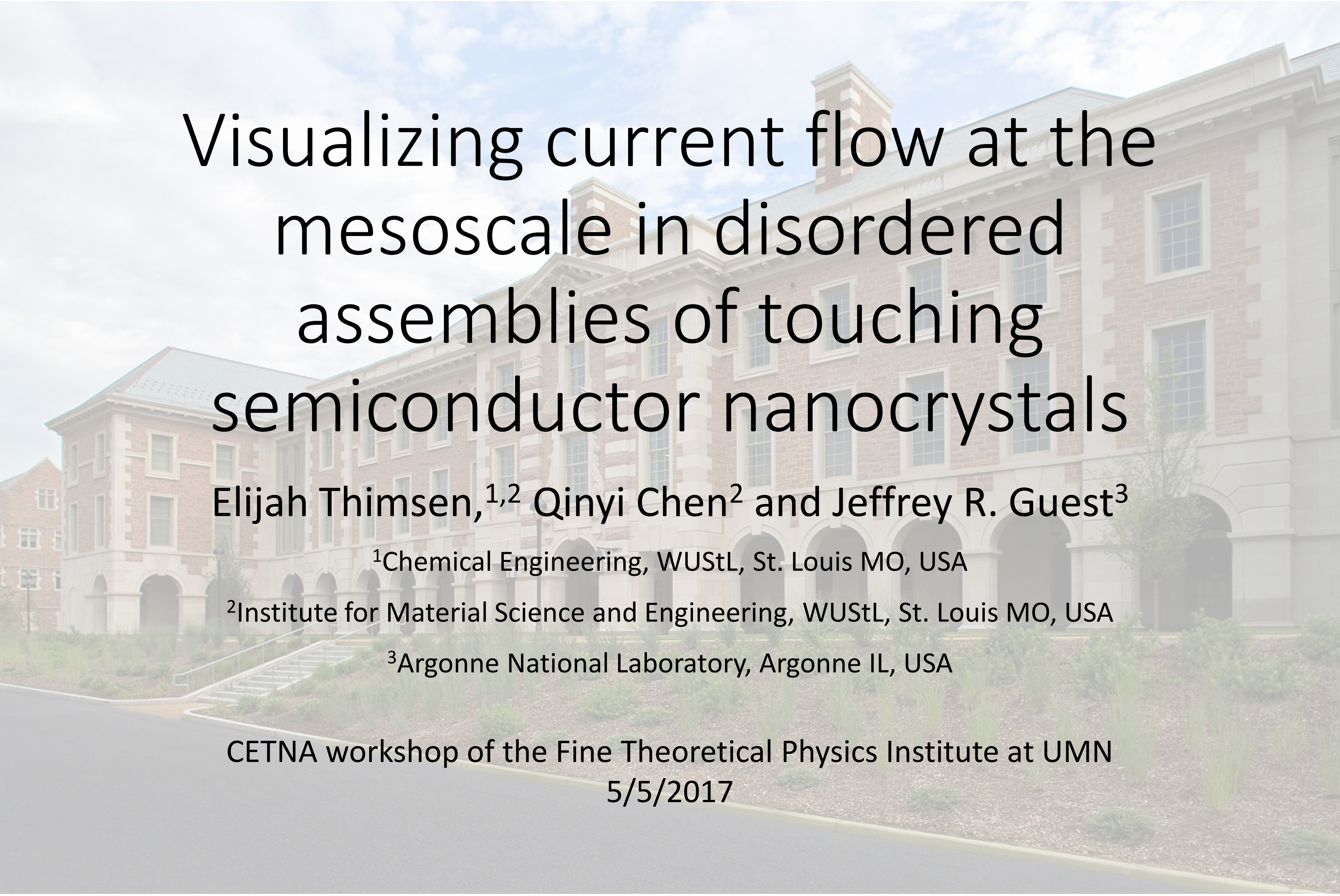

Visualizing current flow at the mesoscale in disordered assemblies of touching semiconductor nanocrystals

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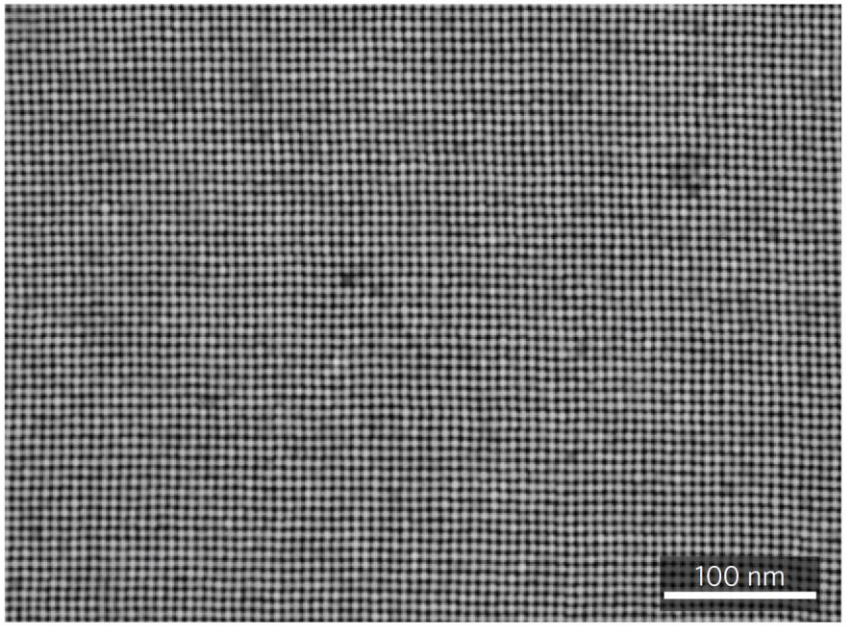
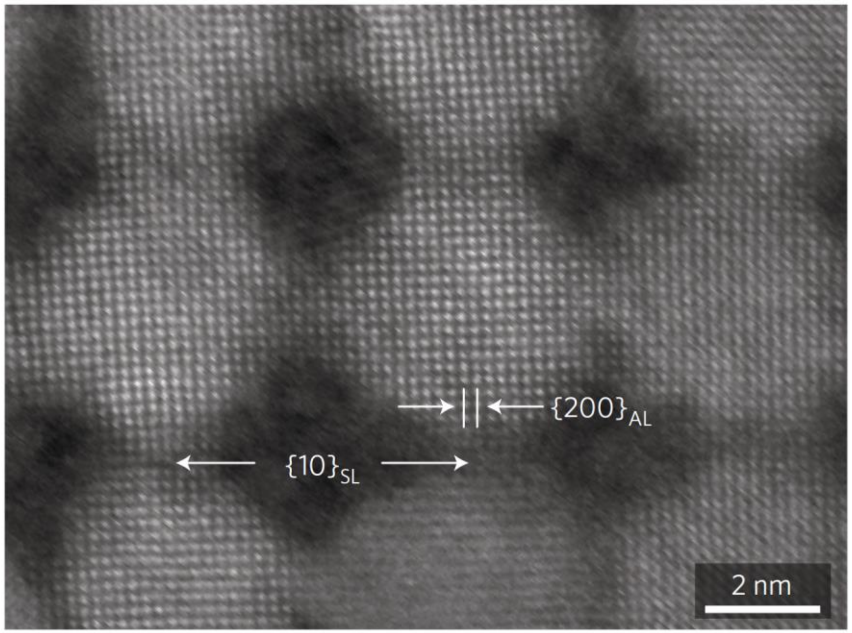
[3]Argonne National Laboratory, Argonne IL, USA

CETNA workshop of the Fine Theoretical Physics Institute at UMN
5/5/2017

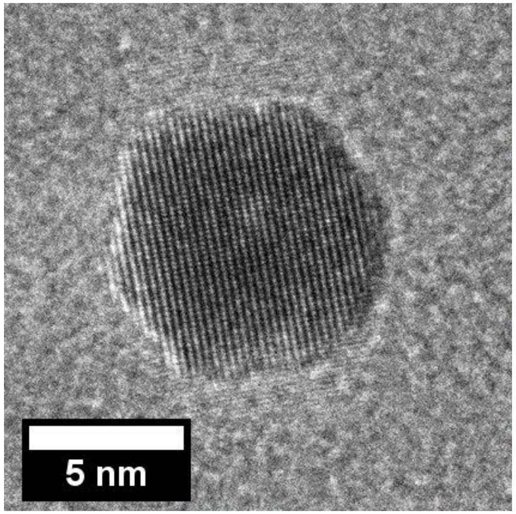
Order, disorder and distributions



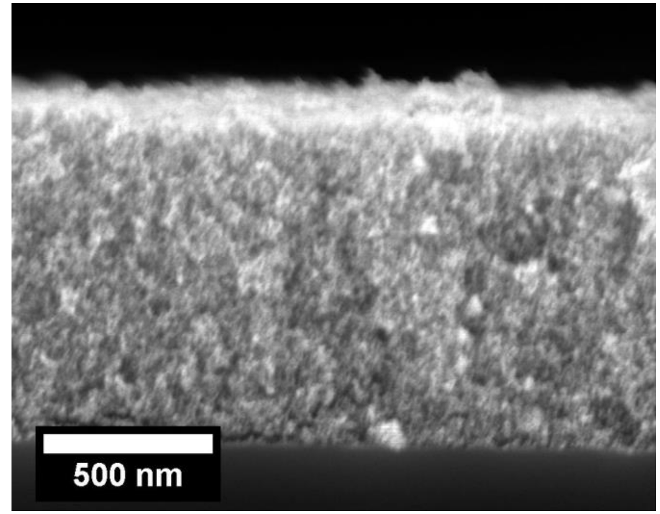


Whitham, K.; Yang, J.; Savitzky, B. H.; Kourkoutis, L. F.; Wise, F.; Hanrath, T. Charge transport and localization in atomically coherent quantum dot solids. *Nat Mater 2016, 15, 557-563.*

Multiscale problem

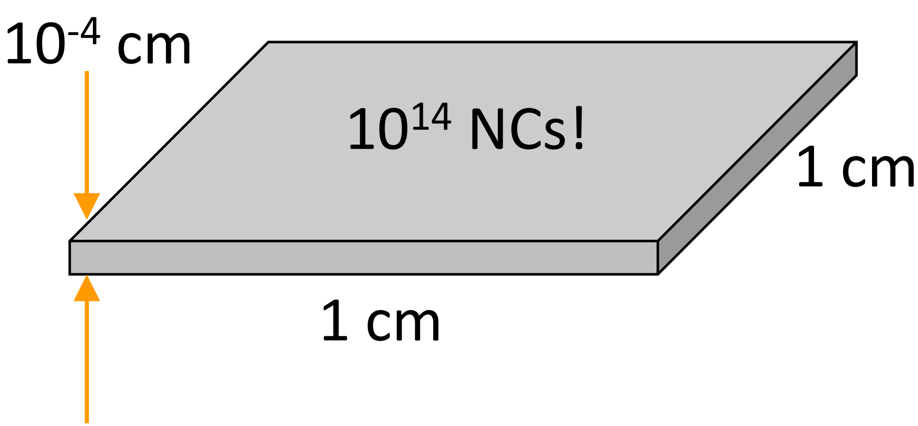


10^{-6} cm

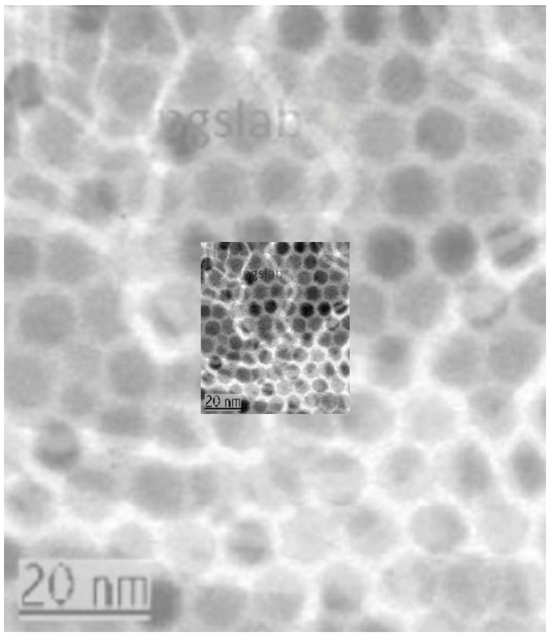


10^{-4} cm

1 cm



Visualizing current flow at the mesoscale



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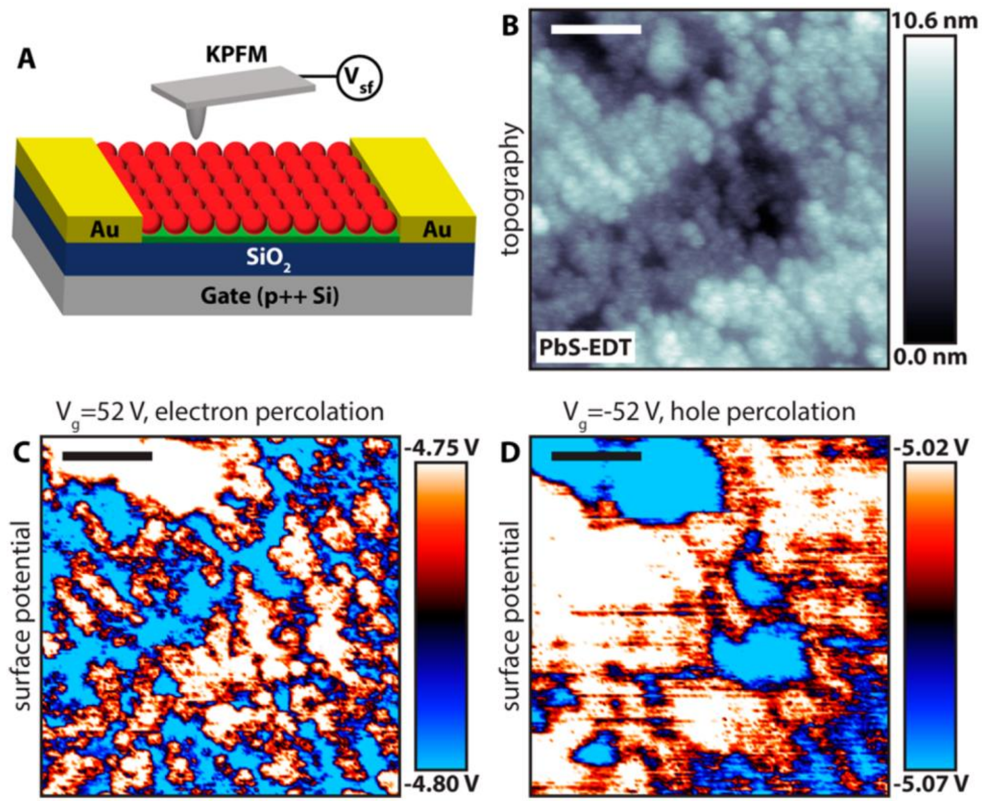

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Long range tunneling and blinking

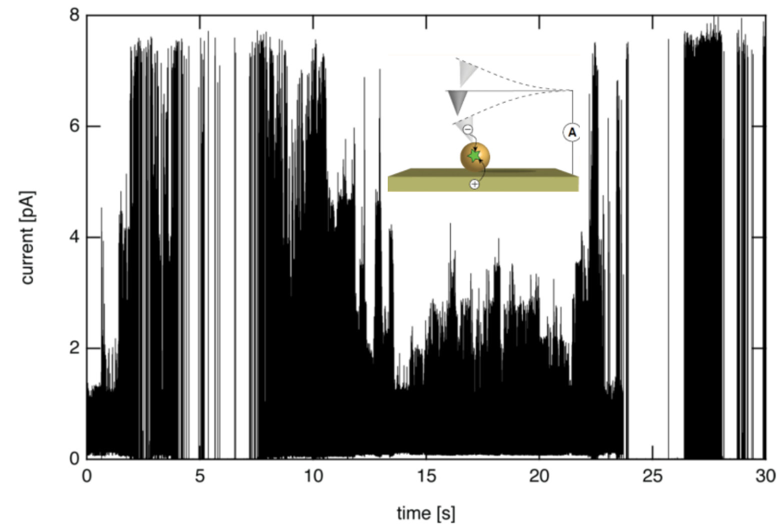
ES-VRH[1]

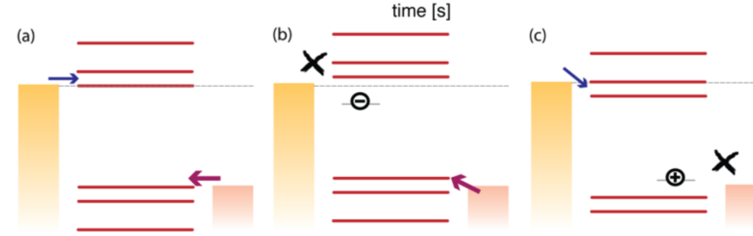
$$R_{ij} = R_0 \exp\left(\frac{2r_{ij}}{\xi} + \frac{\varepsilon_{ij}}{k_B T}\right)$$

$$\varepsilon_{ij} = \left|\varepsilon_i - \varepsilon_j\right| - E_c$$

In our materials, ξ from 31 to 64 nm

Current blinking[2,3,4]





4. Maturova, K.; Nanayakkara, S. U.; Luther, J. M.; van de Lagemaat, J. Fast Current Blinking in Individual PbS and CdSe Quantum Dots. *Nano. Lett. 2013, 13, 2338-2345.*

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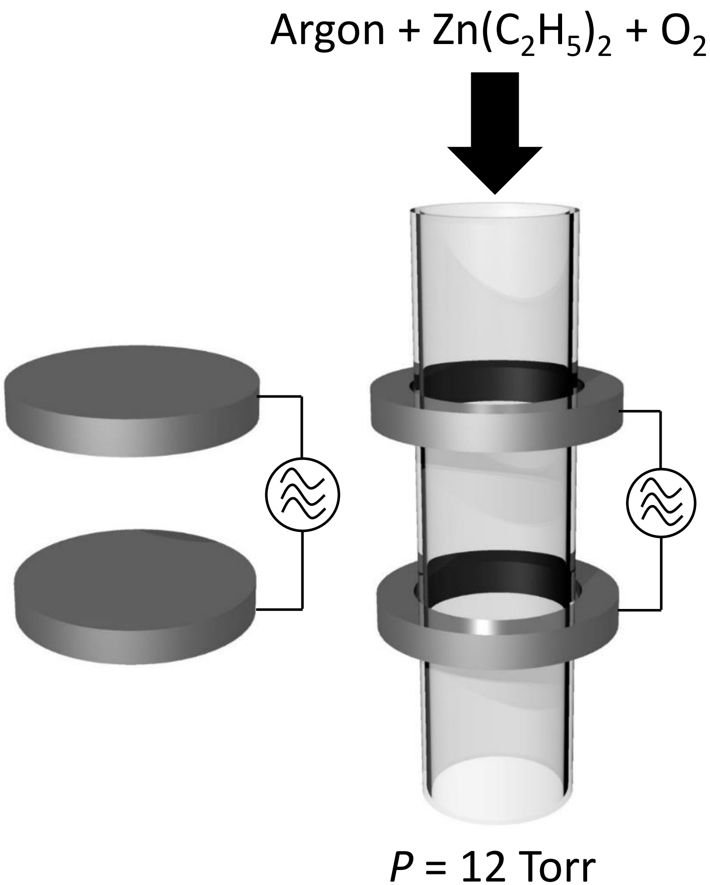
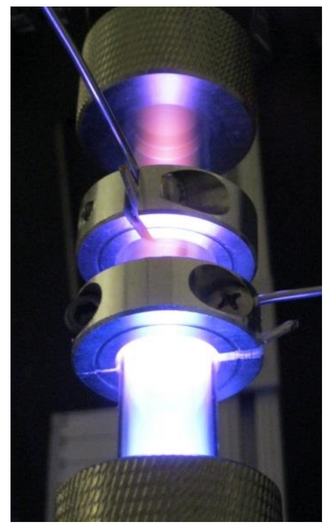
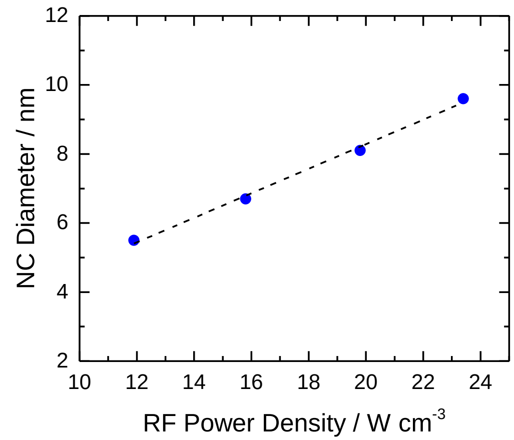
Outline

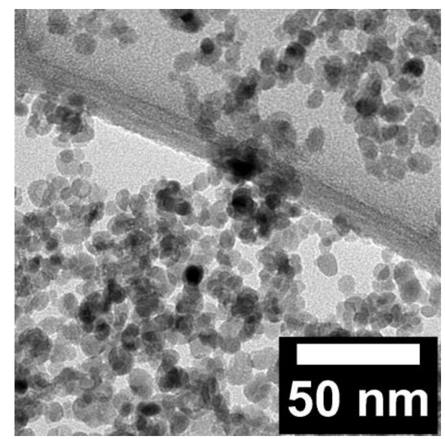
1. Sample preparation
2. Control of transport mechanism
3. Visualization of current flow

Plasma synthesis of ZnO NCs









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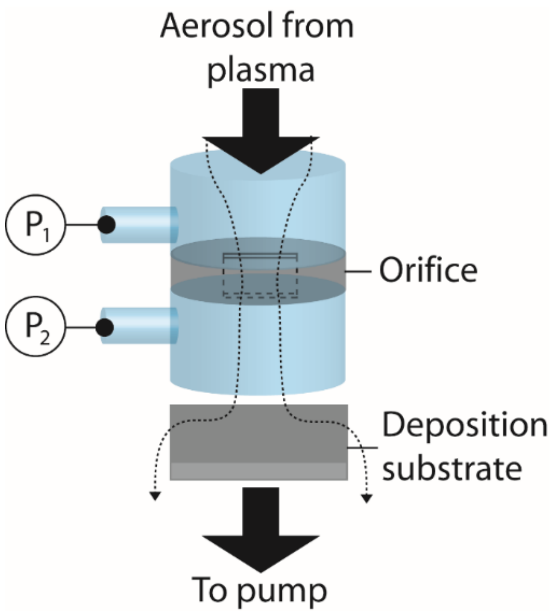
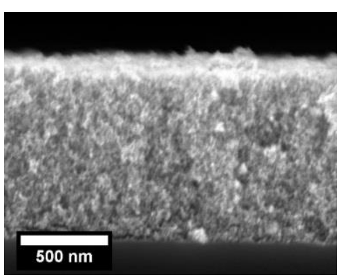
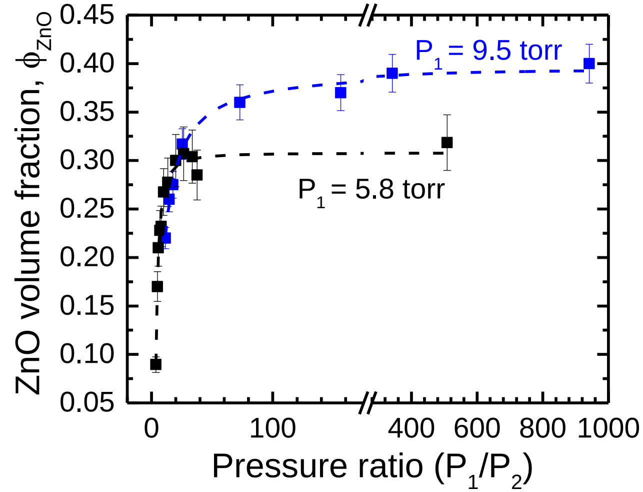
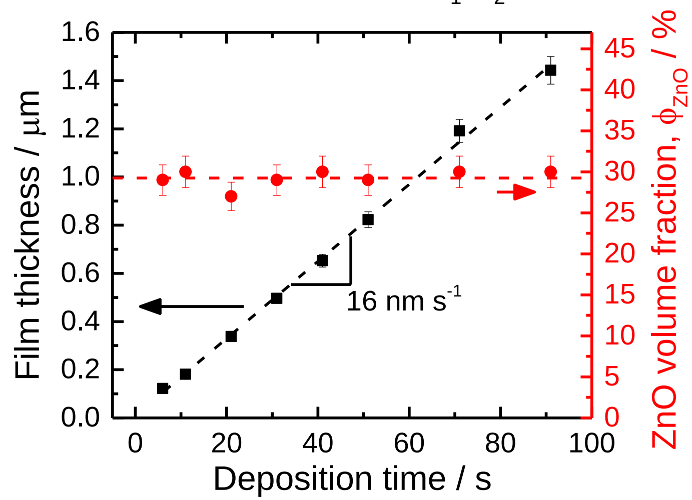
NC deposition by supersonic impact









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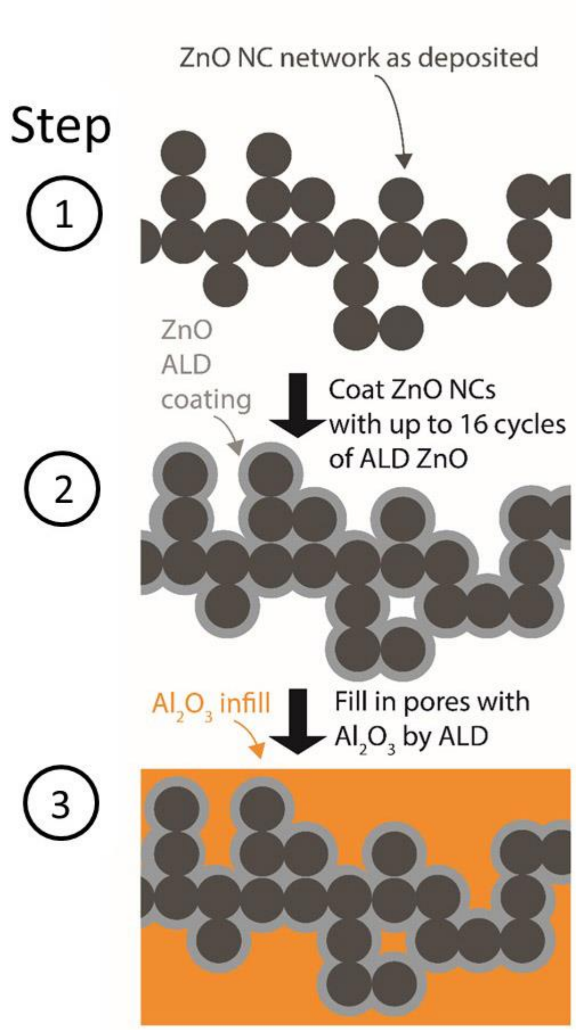
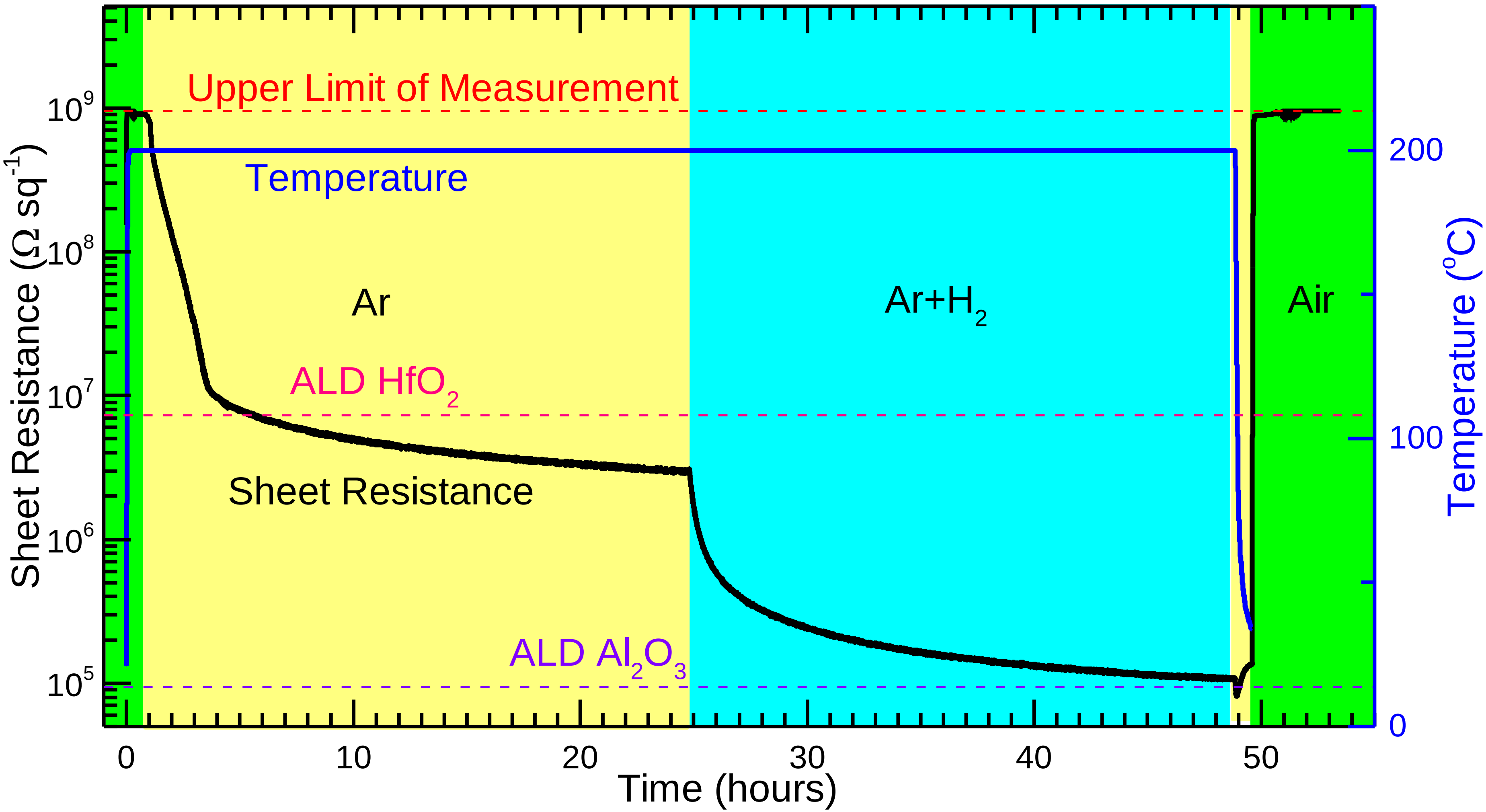
Surface preparation by atomic layer deposition



1. Lanigan, D.; Thimsen, E. Contact Radius and the Insulator–Metal Transition in Films Comprised of Touching Semiconductor Nanocrystals. *ACS Nano 2016, 10, 6744-6752.*

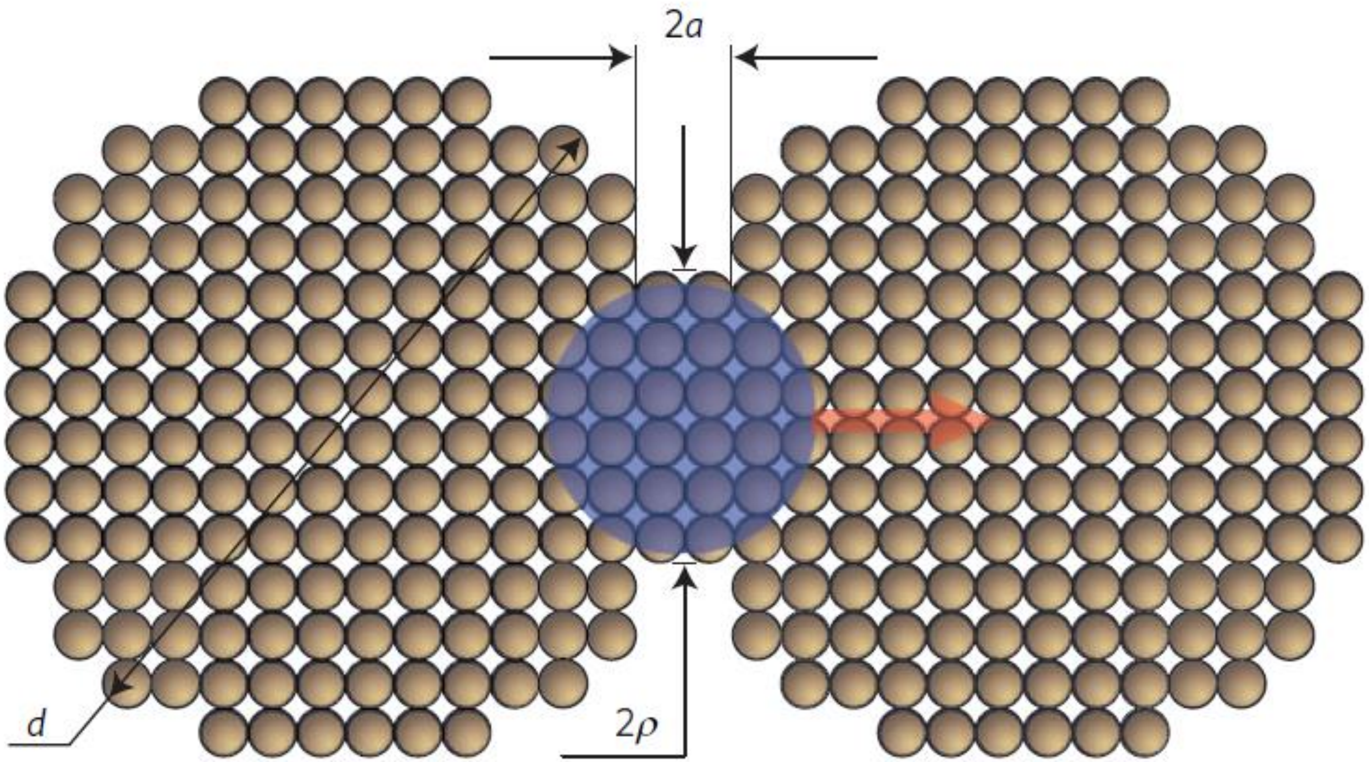
2. Thimsen, E.; Johnson, M.; Zhang, X.; Wagner, A. J.; Mkhoyan, K. A.; Kortshagen, U. R.; Aydil, E. S. High electron mobility in thin films formed via supersonic impact deposition of nanocrystals synthesized in nonthermal plasmas. *Nat Commun 2014, 5, 5822.*

Al_2O_3 coating reduces ZnO superficially



Ephraim, J.; Lanigan, D.; Staller, C.; Milliron, D. J.; Thimsen, E. Transparent Conductive Oxide Nanocrystals Coated with Insulators by Atomic Layer Deposition. *Chem. Mater. 2016, 28, 5549-5553.*

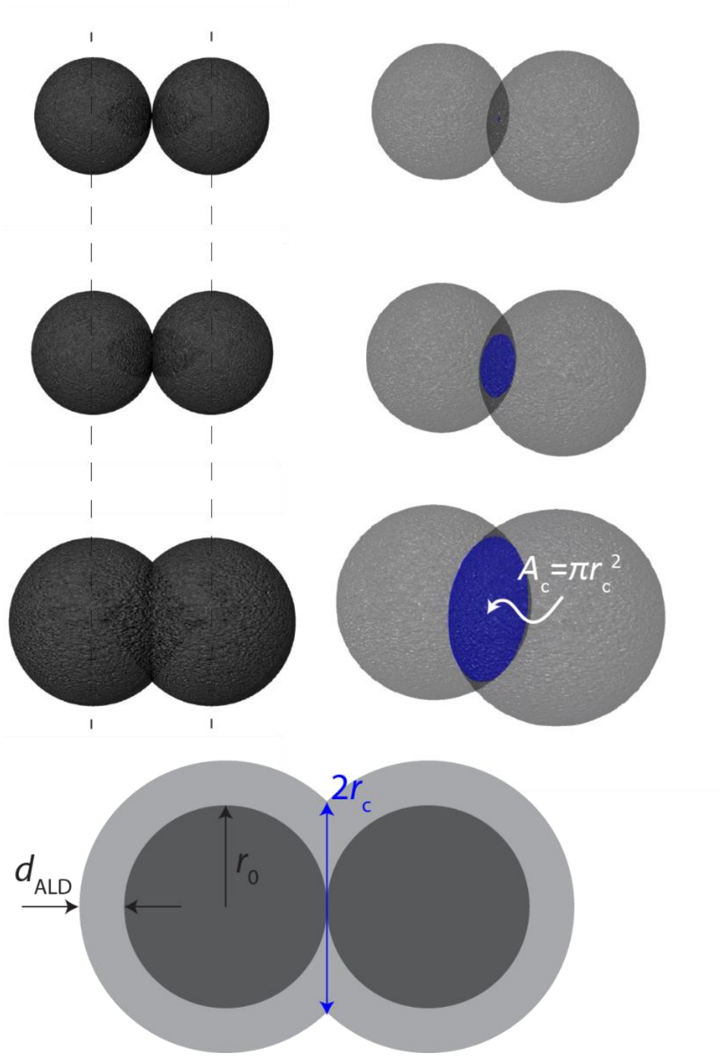
IMT in arrays of touching nanocrystals



$$n_{crit} r_C^3 \approx 0.3g$$

Chen, T.; Reich, K. V.; Kramer, N. J.; Fu, H.; Kortshagen, U. R.; Shklovskii, B. I., *Nat. Mater.* ***2016****, 15, (3), 299.*
Beloborodov, I. S.; Lopatin, A. V.; Vinokur, V. M.; Efetov, K. B.; *Rev. Mod. Phys.* ***2007****, 79, (2), 469-518.*

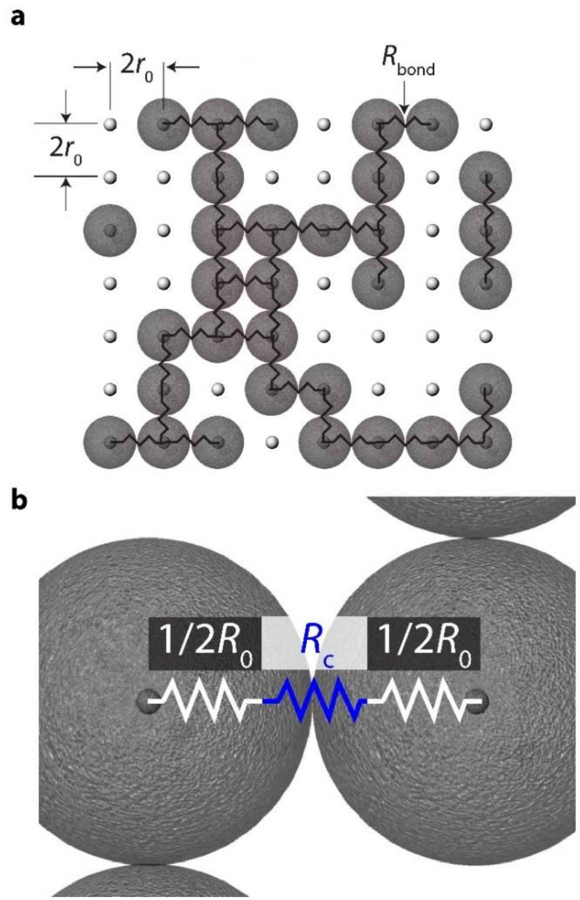
ZnO coating adjusts interparticle contact radius



$$r_C = \sqrt{d_{ALD}^2 + 2r_0 d_{ALD}}$$

Lanigan, D.; Thimsen, E. Contact Radius and the Insulator–Metal Transition in Films Comprised of Touching Semiconductor Nanocrystals. *ACS Nano 2016, 10, 6744-6752.*

An alternative way of calculating contact radius



$$R_{bond} = \frac{\rho \cdot (\phi - \phi_0)^{1.9}}{2r_0}$$

$$R_{bond} = R_0 + R_C$$

$$R_0 = \frac{\hbar^2 \pi^{1/3} 3^{2/3}}{8e\, m_e k_B} \cdot \frac{1}{r_0 n^{1/3} T \mu_{local}}$$

$$r_C = \sqrt{\frac{4\pi\hbar}{R_C e^2 k_F^2}}$$

$$k_F = \left(\frac{3\pi^2}{g} n\right)^{1/3}$$

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2. Lanigan, D.; Thimsen, E. Contact Radius and the Insulator–Metal Transition in Films Comprised of Touching Semiconductor Nanocrystals. *ACS Nano 2016, 10, 6744-6752.*
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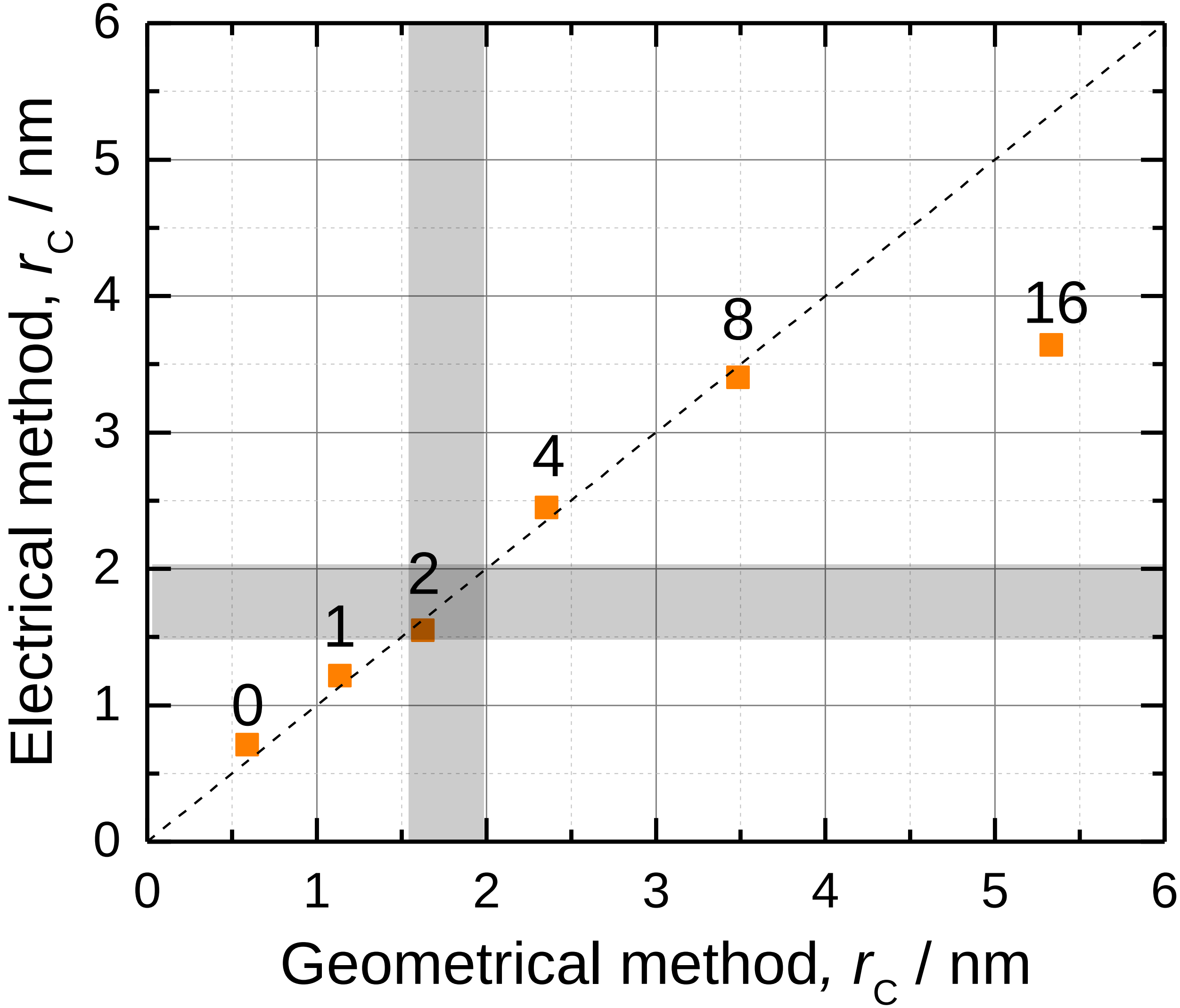
4. Chen, T.; Reich, K. V.; Kramer, N. J.; Fu, H.; Kortshagen, U. R.; Shklovskii, B. I., *Nat. Mater.* ***2016**, 15, (3), 299.*

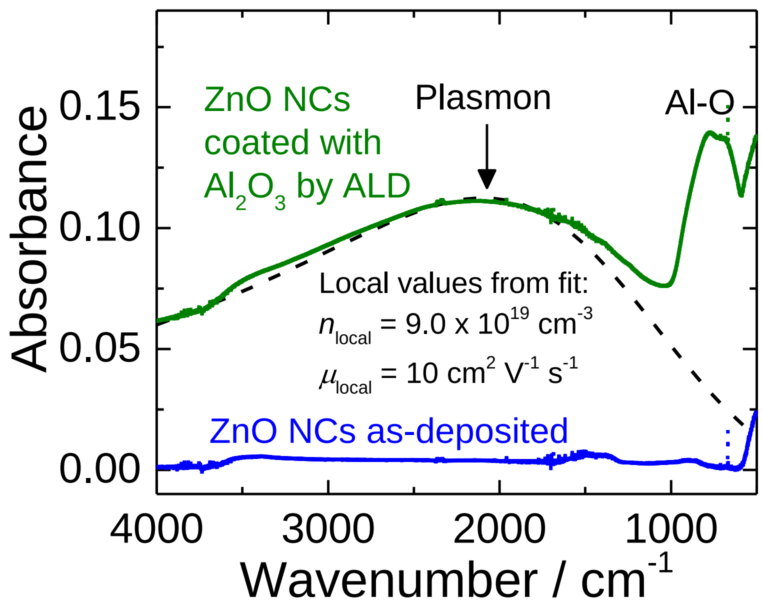
Comparison between methods



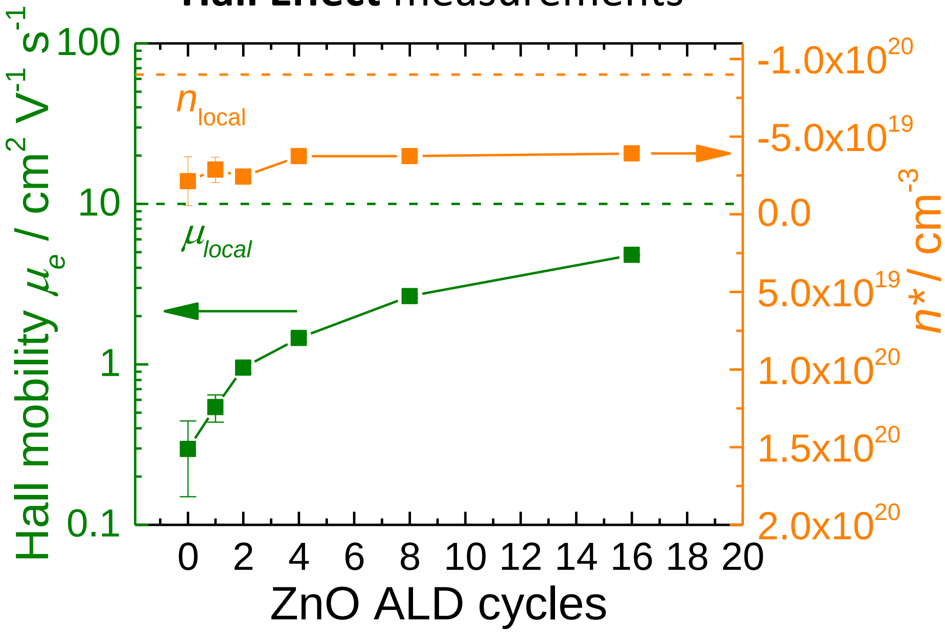
Lanigan, D.; Thimsen, E. Contact Radius and the Insulator–Metal Transition in Films Comprised of Touching Semiconductor Nanocrystals. *ACS Nano 2016, 10, 6744-6752.*

Contact radius controls carrier mobility

Local mobility and carrier concentration from **IR absorption**

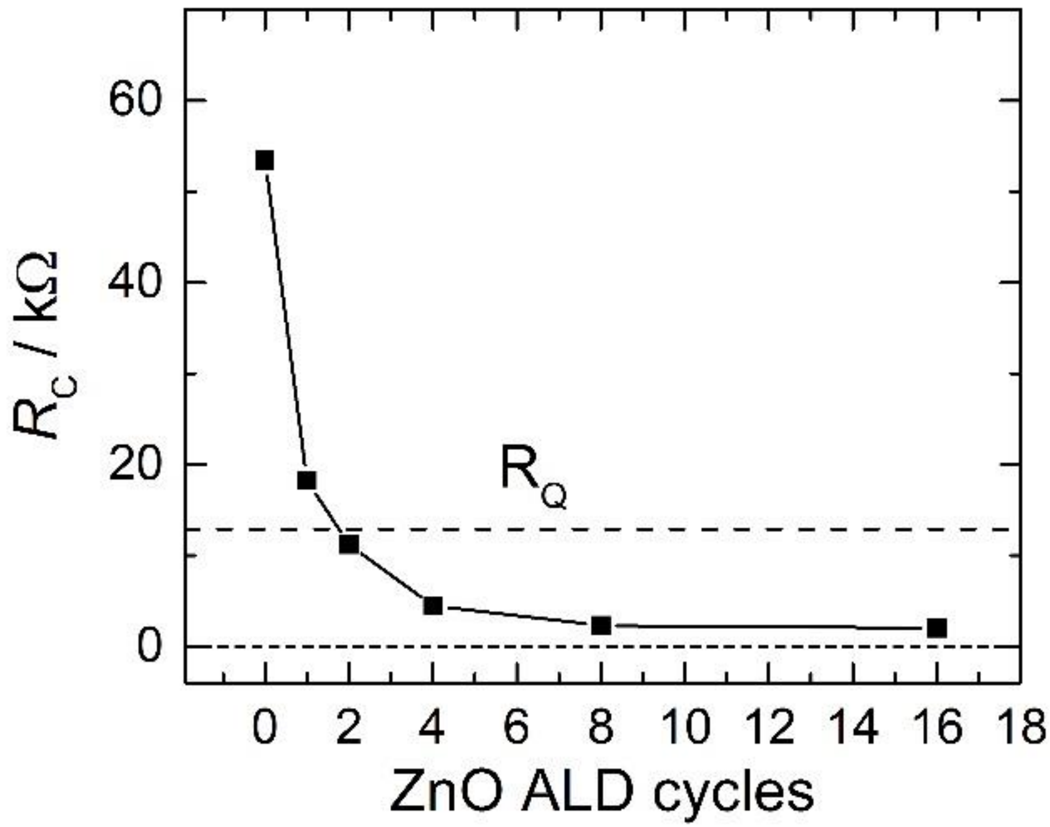


Longitudinal mobility and carrier concentration from **Hall Effect** measurements



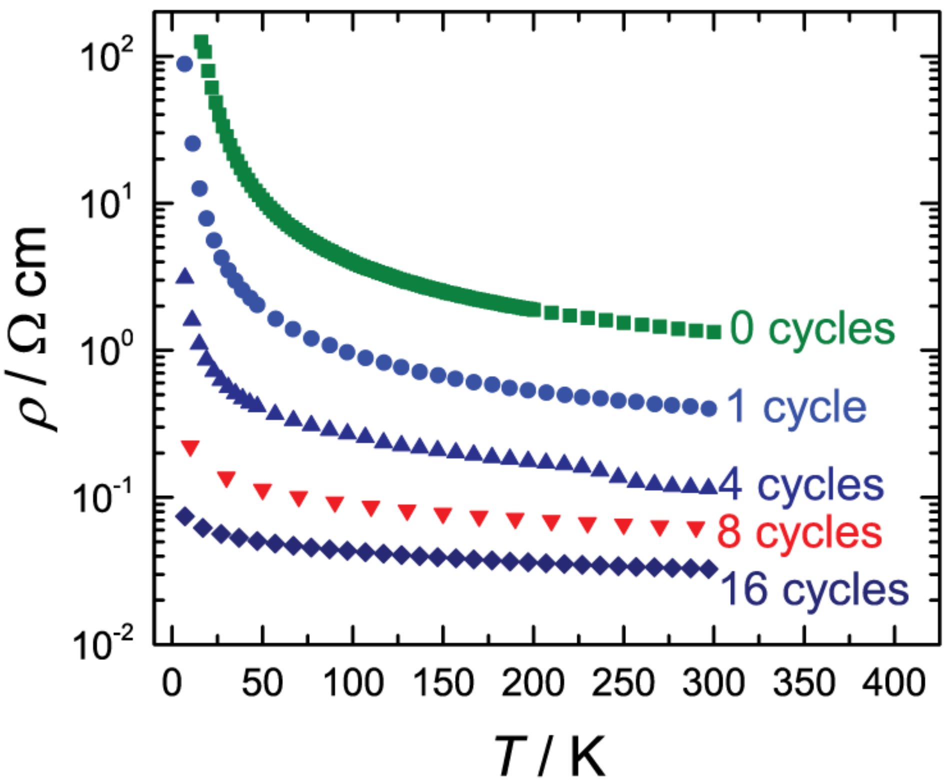
Lanigan, D.; Thimsen, E. Contact Radius and the Insulator–Metal Transition in Films Comprised of Touching Semiconductor Nanocrystals. *ACS Nano 2016, 10, 6744-6752.*

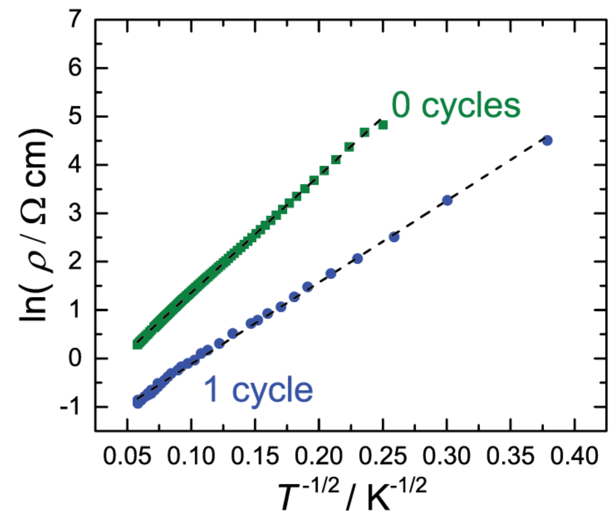
Calculated contact resistance

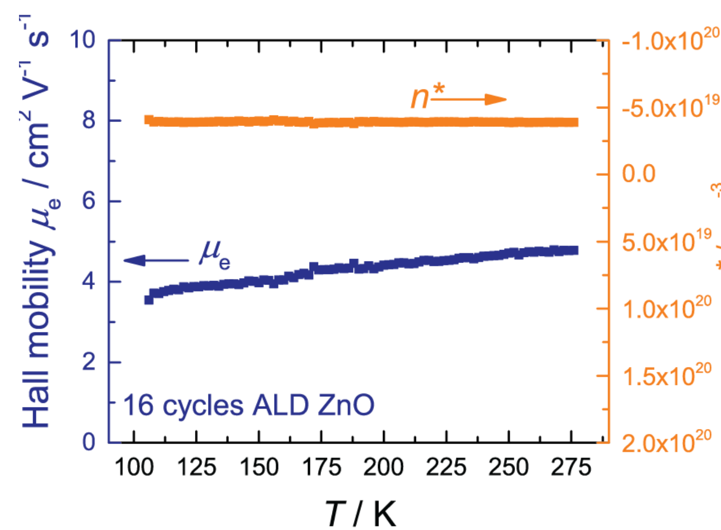


Lanigan, D.; Thimsen, E. Contact Radius and the Insulator–Metal Transition in Films Comprised of Touching Semiconductor Nanocrystals. *ACS Nano 2016, 10, 6744-6752.*

Contact radius and transport mechanism





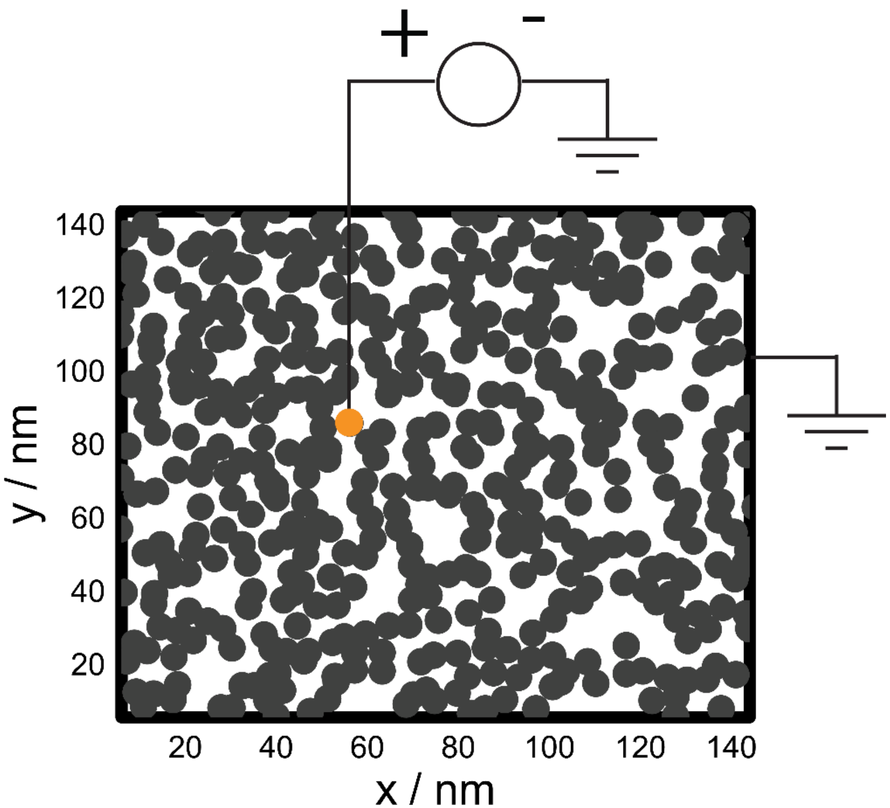


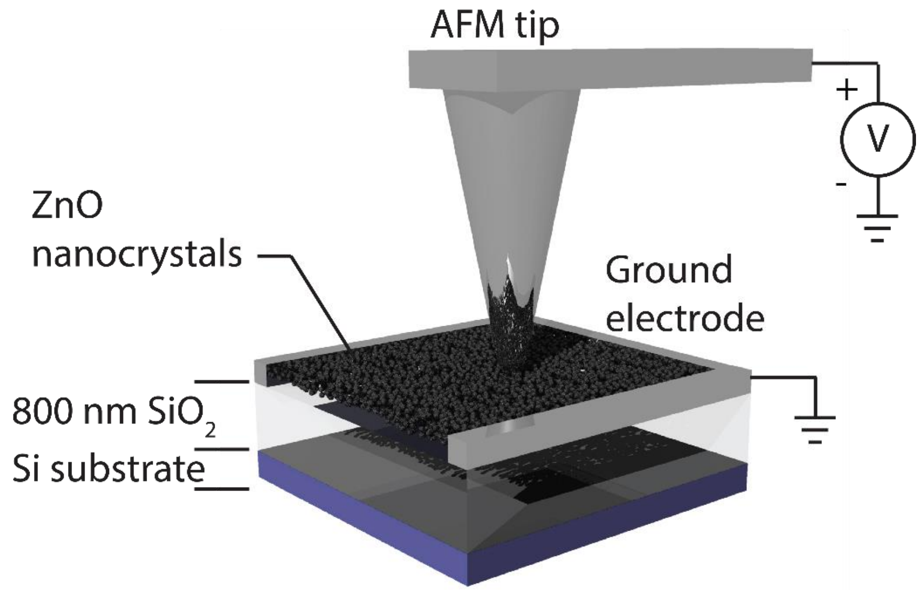
Lanigan, D.; Thimsen, E. Contact Radius and the Insulator–Metal Transition in Films Comprised of Touching Semiconductor Nanocrystals. *ACS Nano 2016, 10, 6744-6752.*

Intermediate conclusions

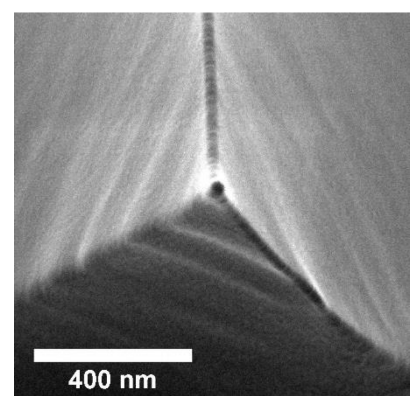
- Coating of ZnO nanocrystals with Al_2O_3 by atomic layer deposition results in a reduction that increases the carrier concentration.
- The electron transport mechanism can be controlled by coating the ZnO nanocrystals with a small amount of ZnO by atomic layer deposition.

Visualization (model and experiment)



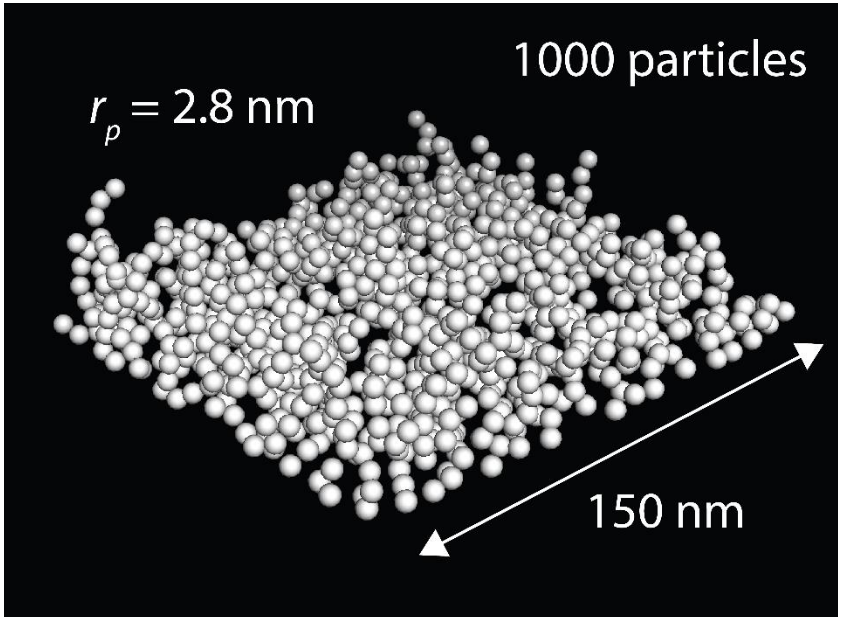


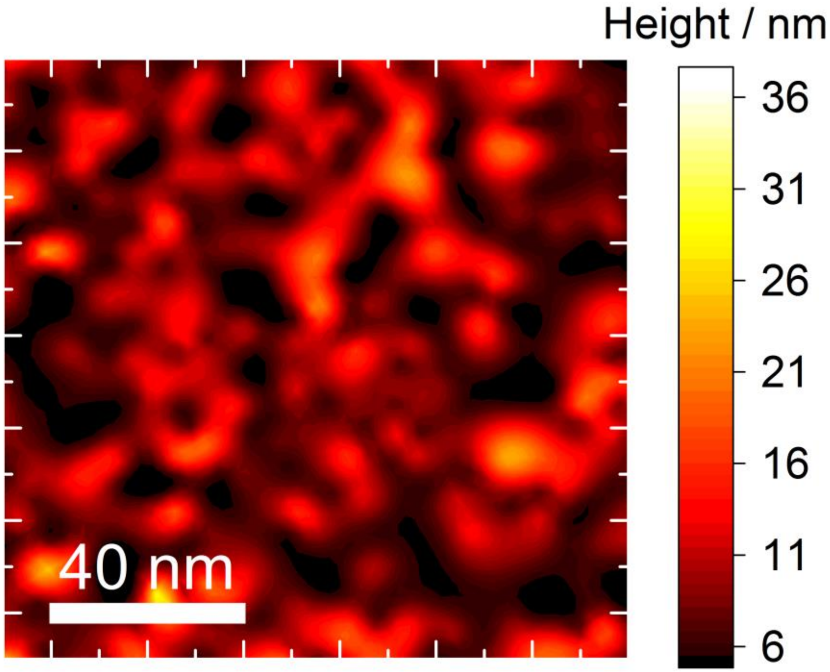
CAFM tip



Chen, Q.; Guest, J.R.; Thimsen, E., Visualizing Current Flow at the Mesoscale in Disordered Assemblies of Touching Semiconductor Nanocrystals. *In Preparation.*

Model NC assembly





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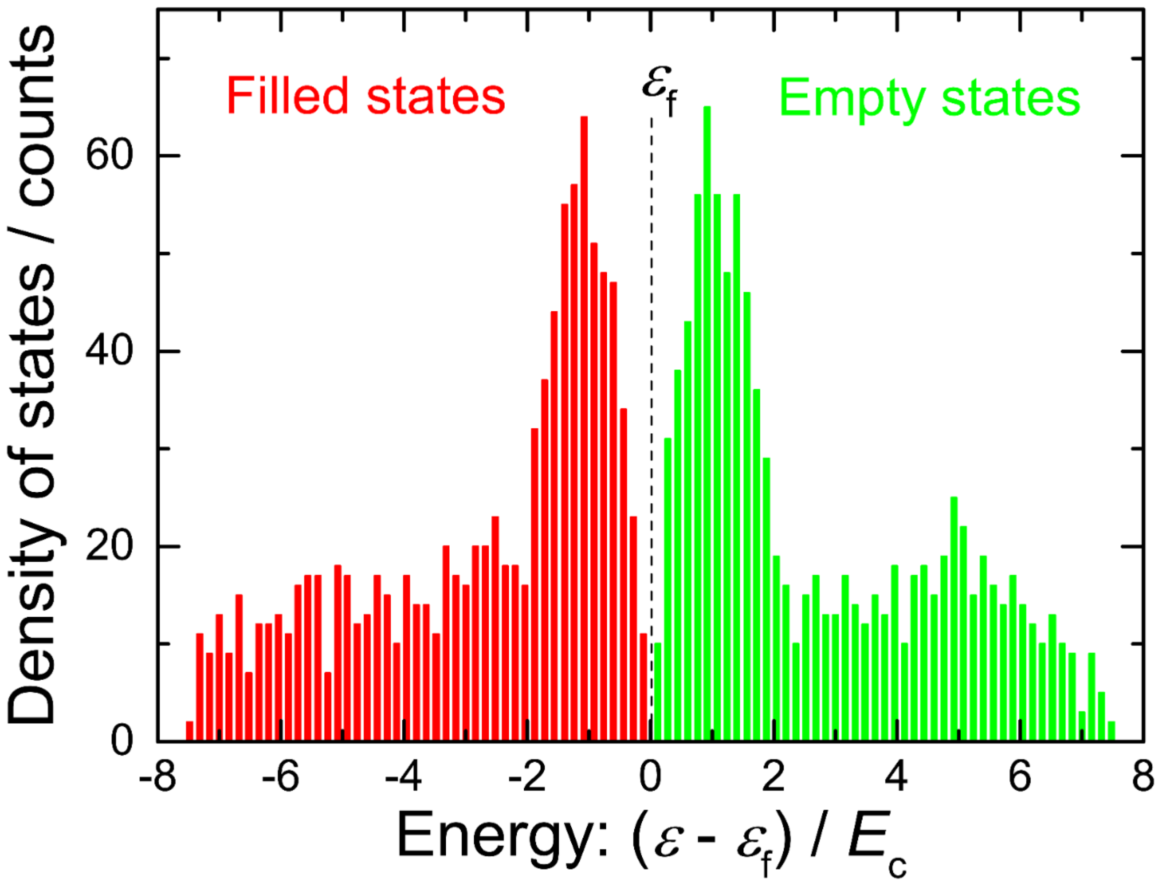
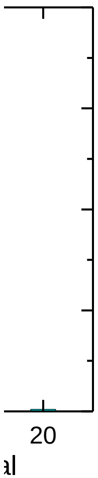
4. Chen, Q.; Guest, J.R.; Thimsen, E., Visualizing Current Flow at the Mesoscale in Disordered Assemblies of Touching Semiconductor Nanocrystals. *In Preparation.*

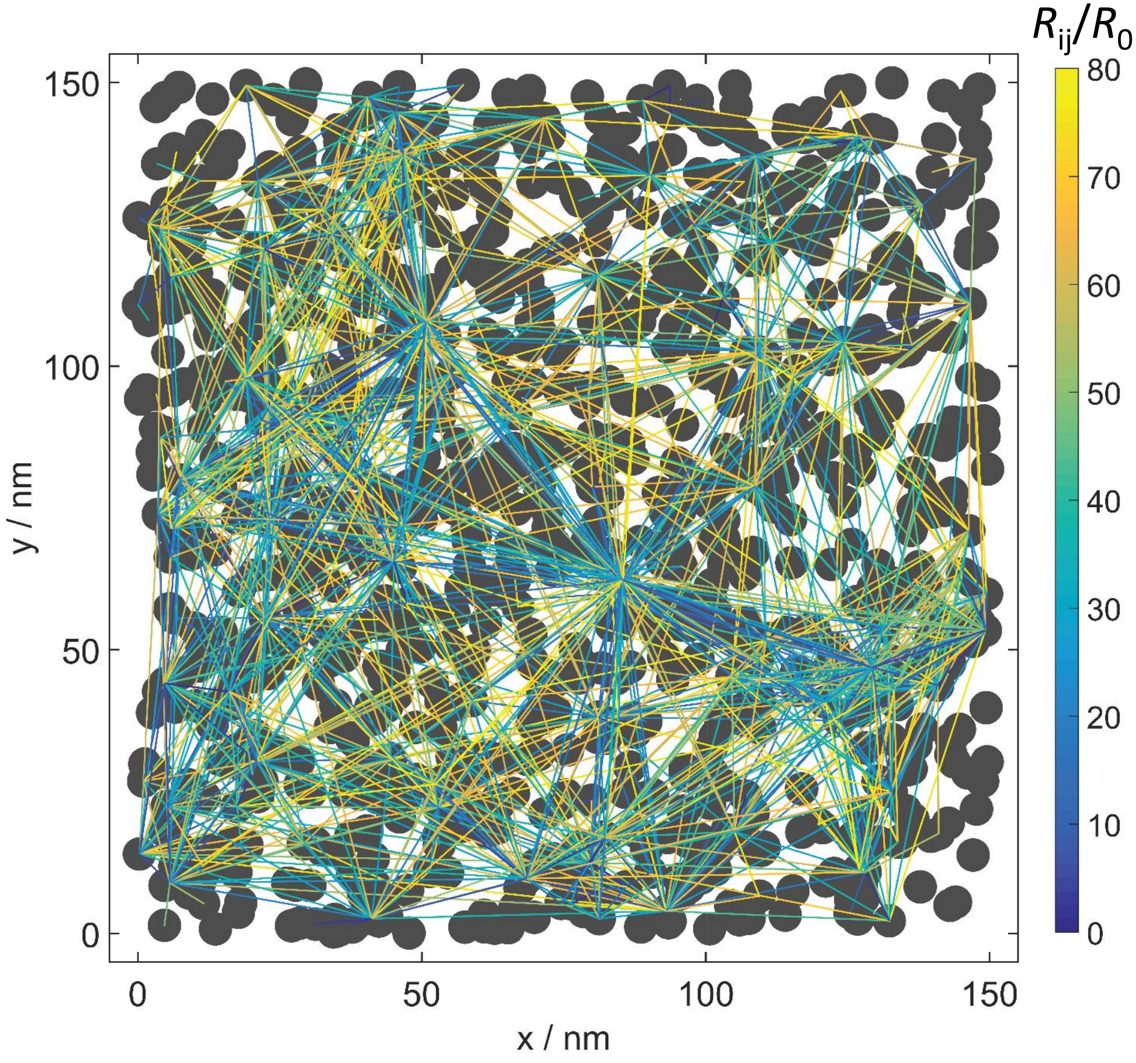
Equilibration





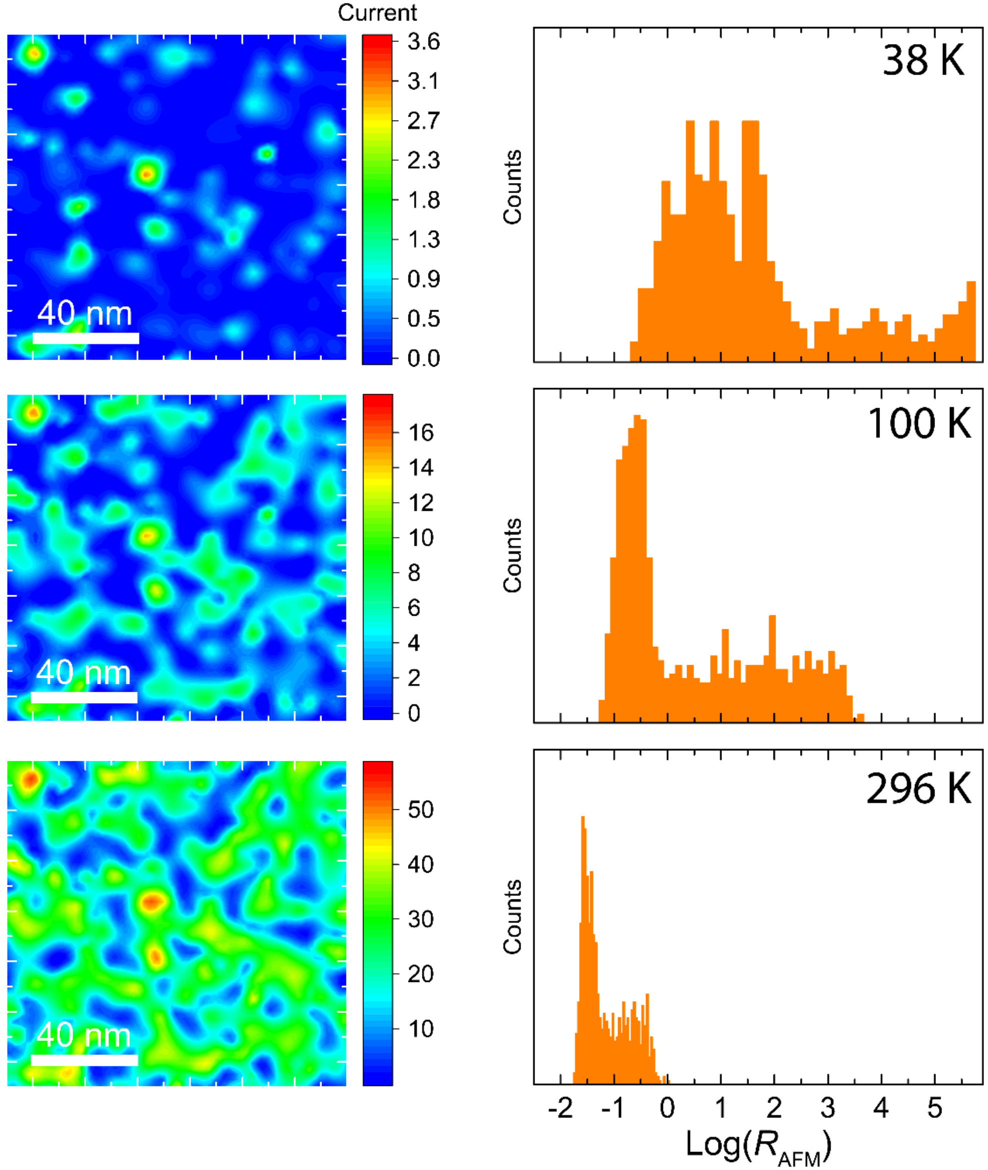
1. Skinner, B.; Chen, T.; Shklovskii, B. I. Theory of hopping conduction in arrays of doped semiconductor nanocrystals. *PRB 2012, 85, 205316.*
2. Chen, Q.; Guest, J.R.; Thimsen, E., Visualizing Current Flow at the Mesoscale in Disordered Assemblies of Touching Semiconductor Nanocrystals. *In Preparation.*

Calculated resistor network (T=38 K)



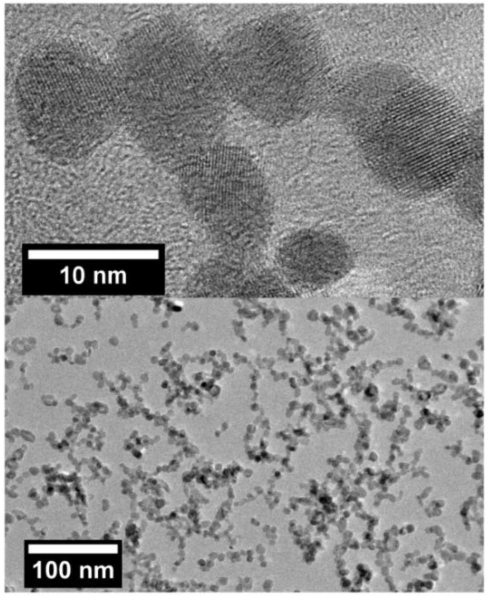
1. Skinner, B.; Chen, T.; Shklovskii, B. I. Theory of hopping conduction in arrays of doped semiconductor nanocrystals. *PRB 2012, 85, 205316.*
2. Chen, Q.; Guest, J.R.; Thimsen, E., Visualizing Current Flow at the Mesoscale in Disordered Assemblies of Touching Semiconductor Nanocrystals. *In Preparation.*

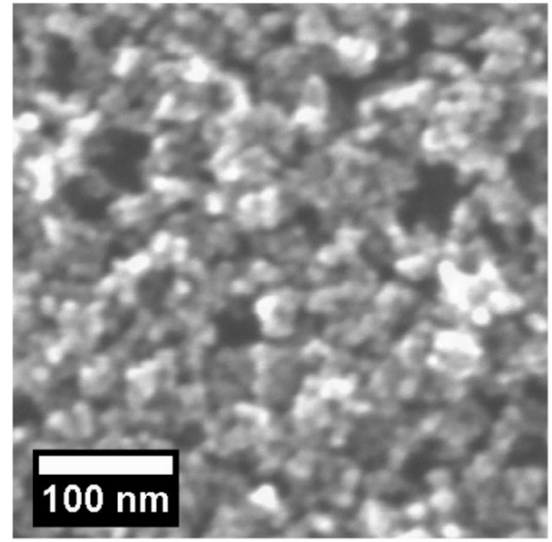
Simulated CAFM current maps

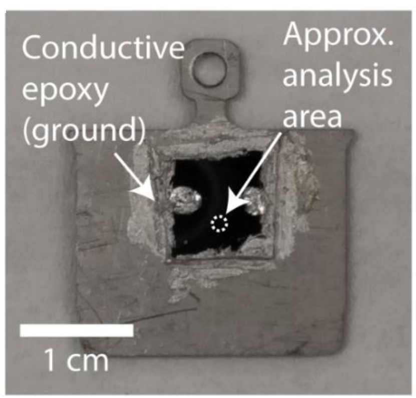


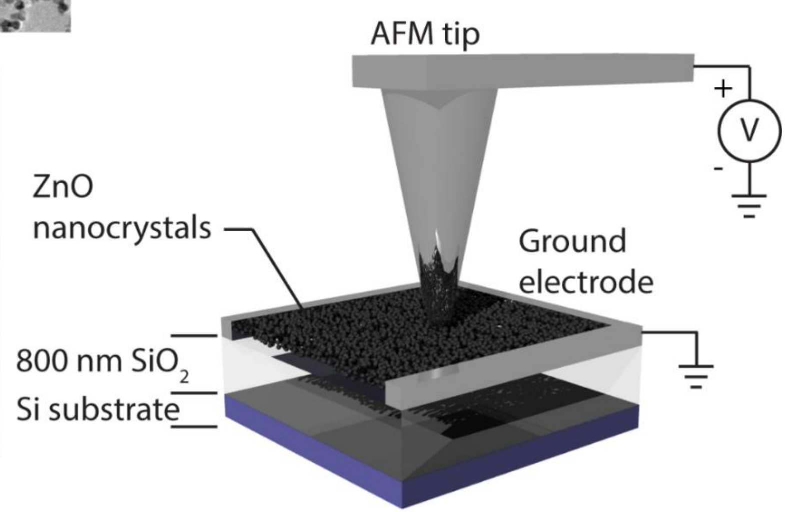
Chen, Q.; Guest, J.R.; Thimsen, E., Visualizing Current Flow at the Mesoscale in Disordered Assemblies of Touching Semiconductor Nanocrystals. *In Preparation.*

Experimental









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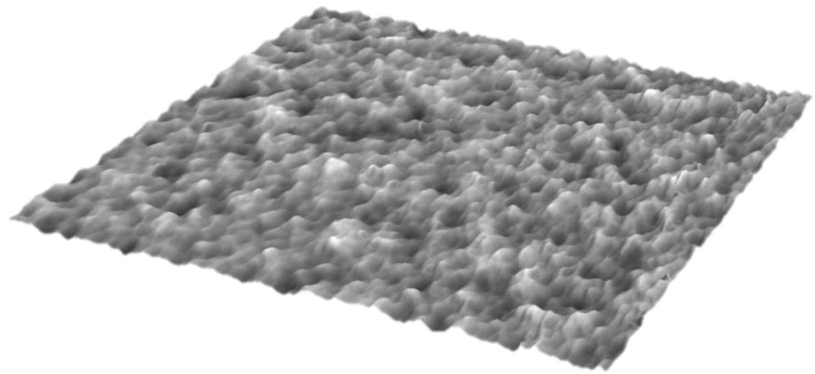
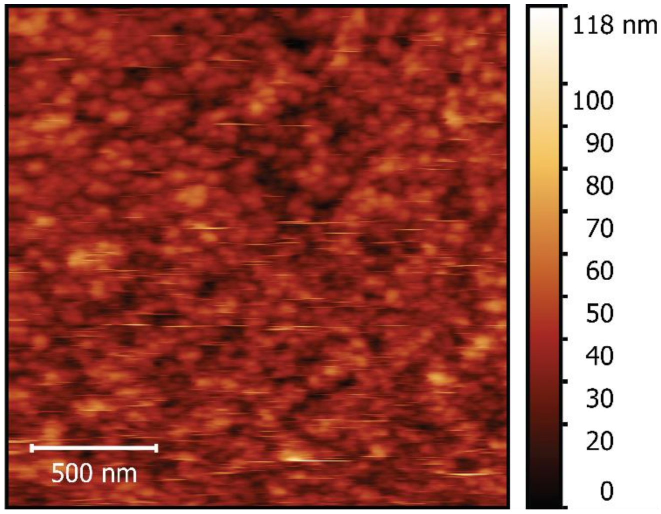
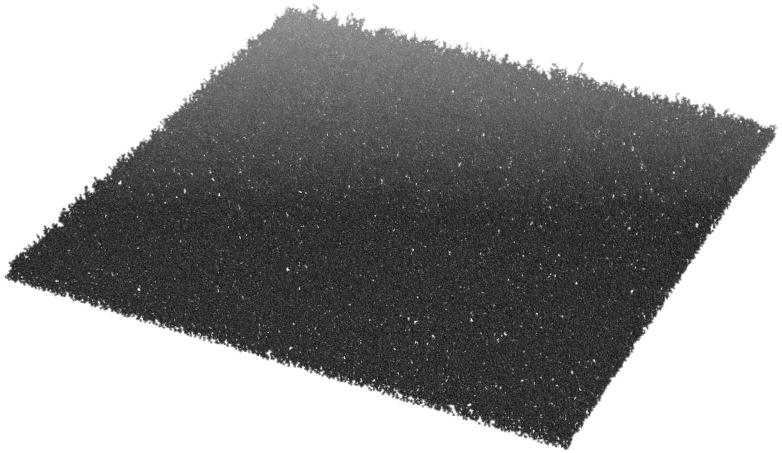
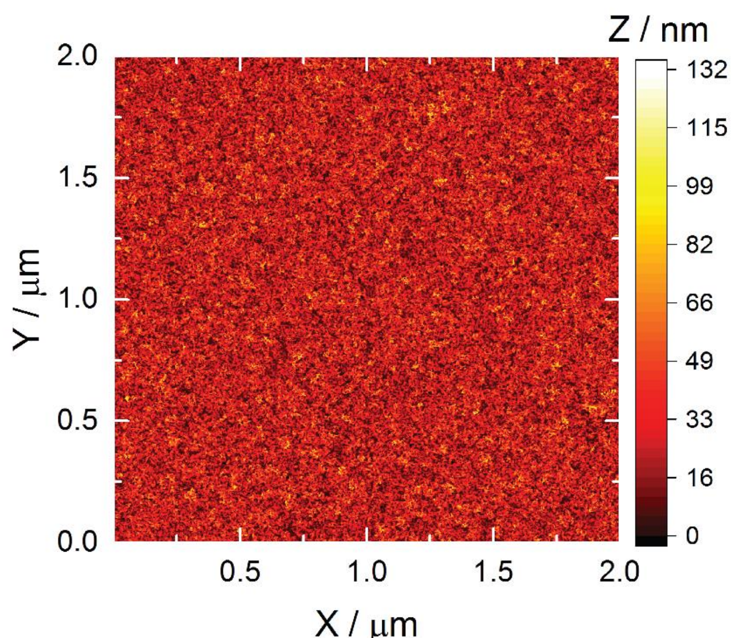
Film structure



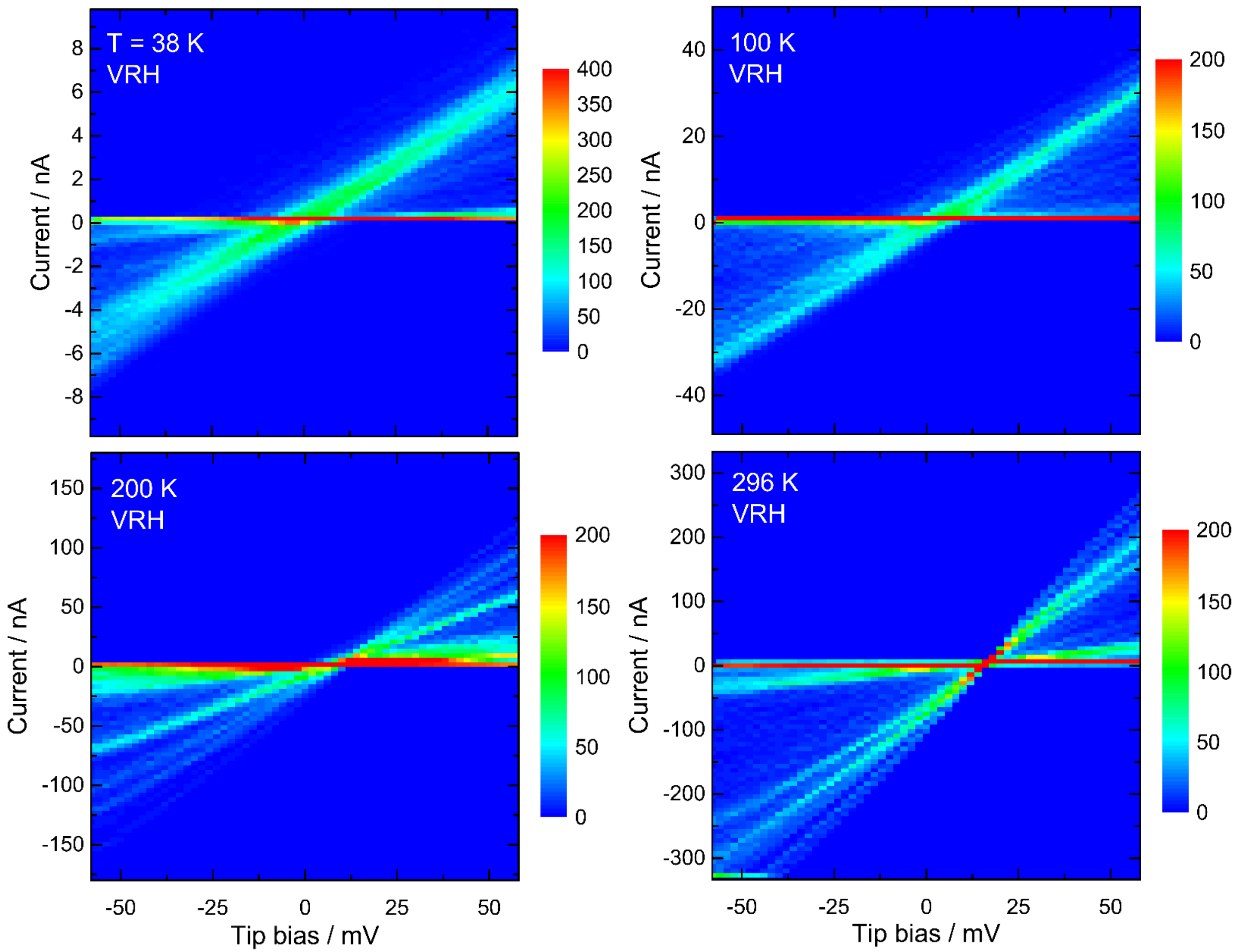






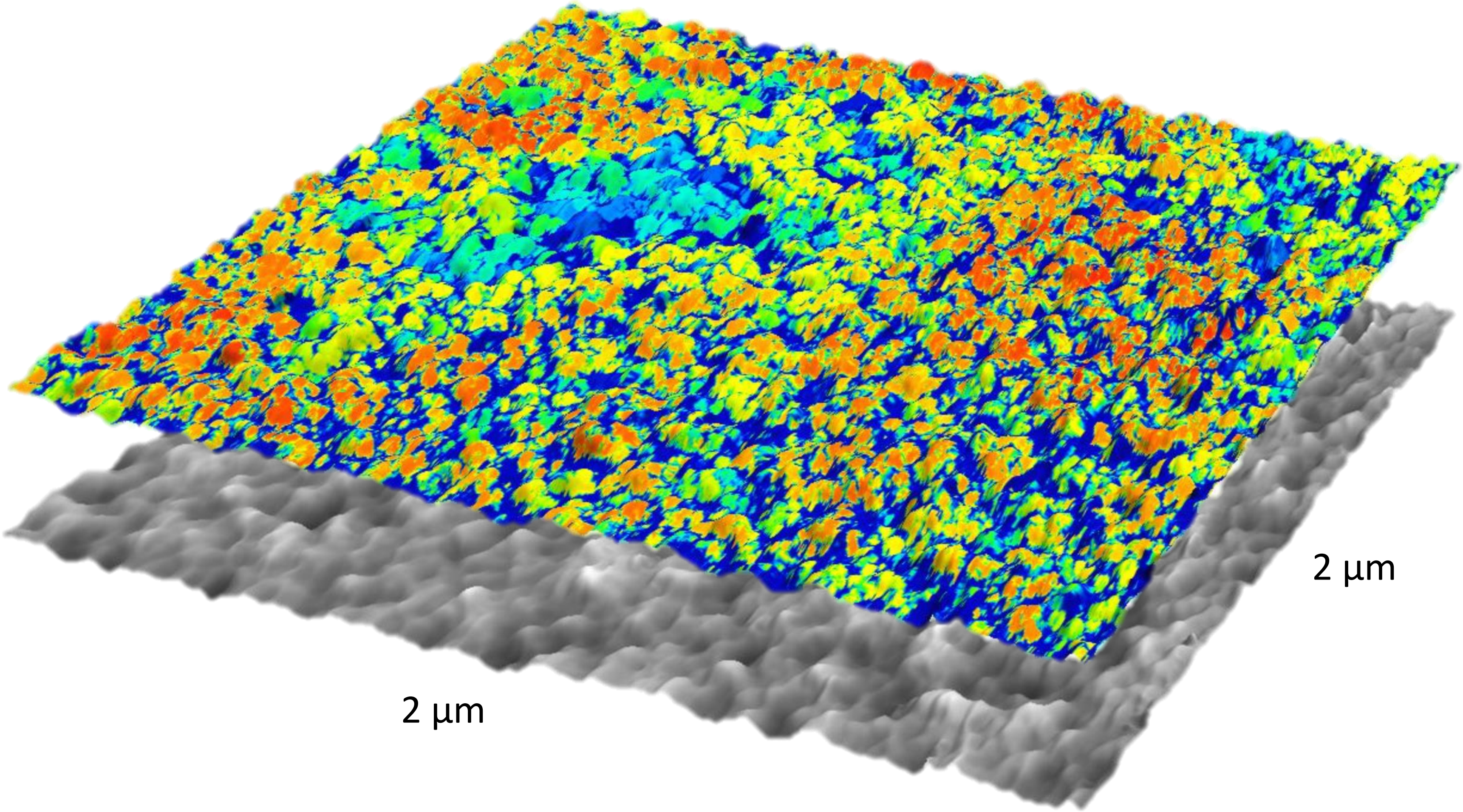
Chen, Q.; Guest, J.R.; Thimsen, E., Visualizing Current Flow at the Mesoscale in Disordered Assemblies of Touching Semiconductor Nanocrystals. *In Preparation.*

Ohmic contact



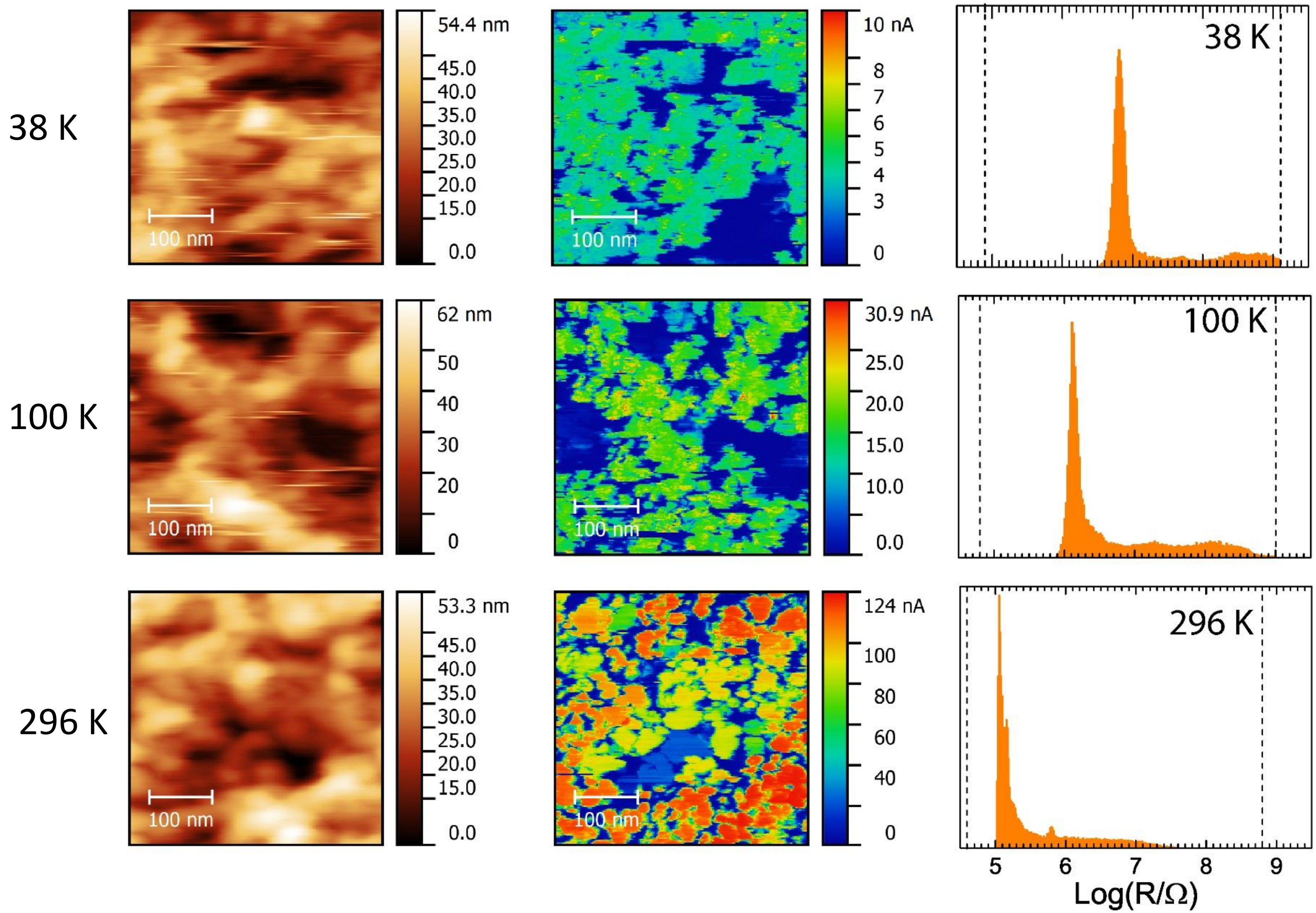
Chen, Q.; Guest, J.R.; Thimsen, E., Visualizing Current Flow at the Mesoscale in Disordered Assemblies of Touching Semiconductor Nanocrystals. *In Preparation.*

Current overlay at *T*=296K



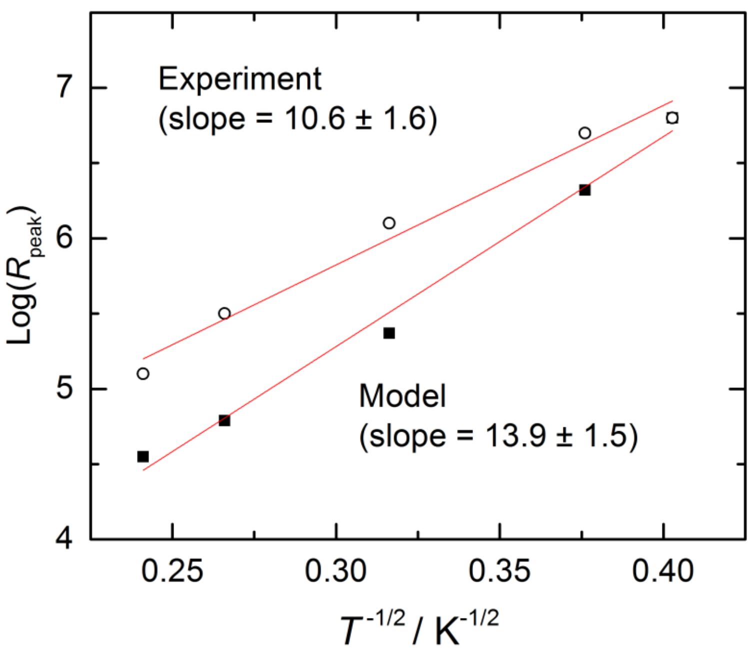
Chen, Q.; Guest, J.R.; Thimsen, E., Visualizing Current Flow at the Mesoscale in Disordered Assemblies of Touching Semiconductor Nanocrystals. *In Preparation.*

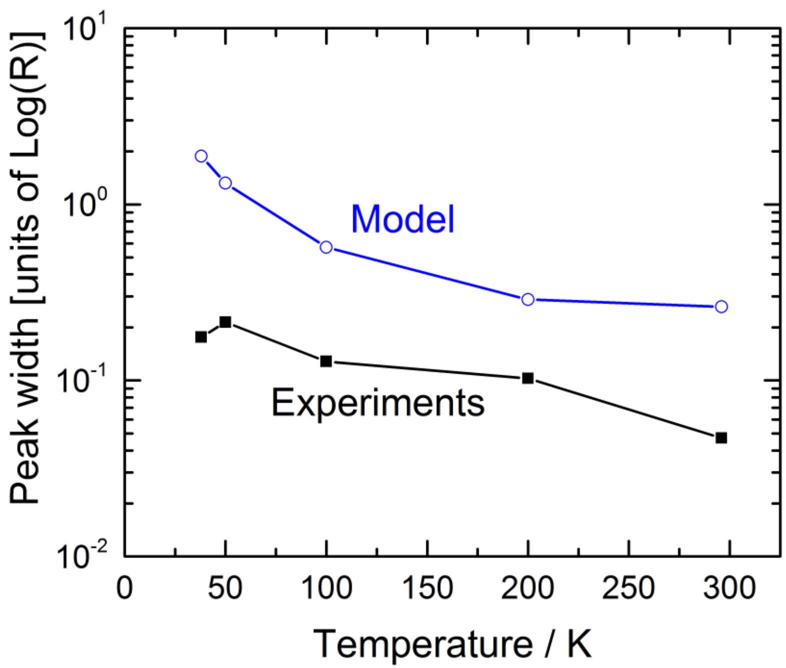
Experimental maps



Chen, Q.; Guest, J.R.; Thimsen, E., Visualizing Current Flow at the Mesoscale in Disordered Assemblies of Touching Semiconductor Nanocrystals. *In Preparation.*

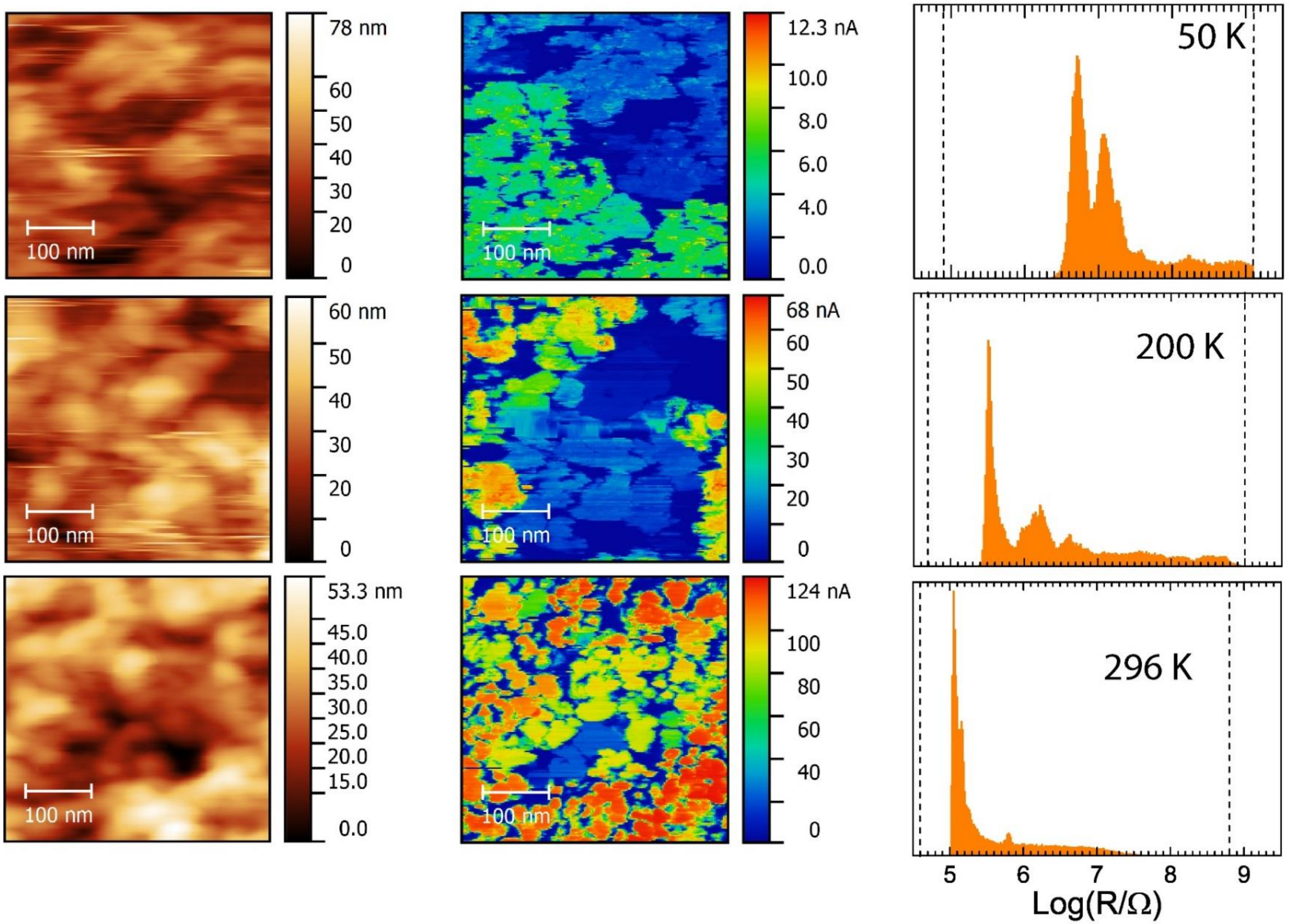
Peak analysis





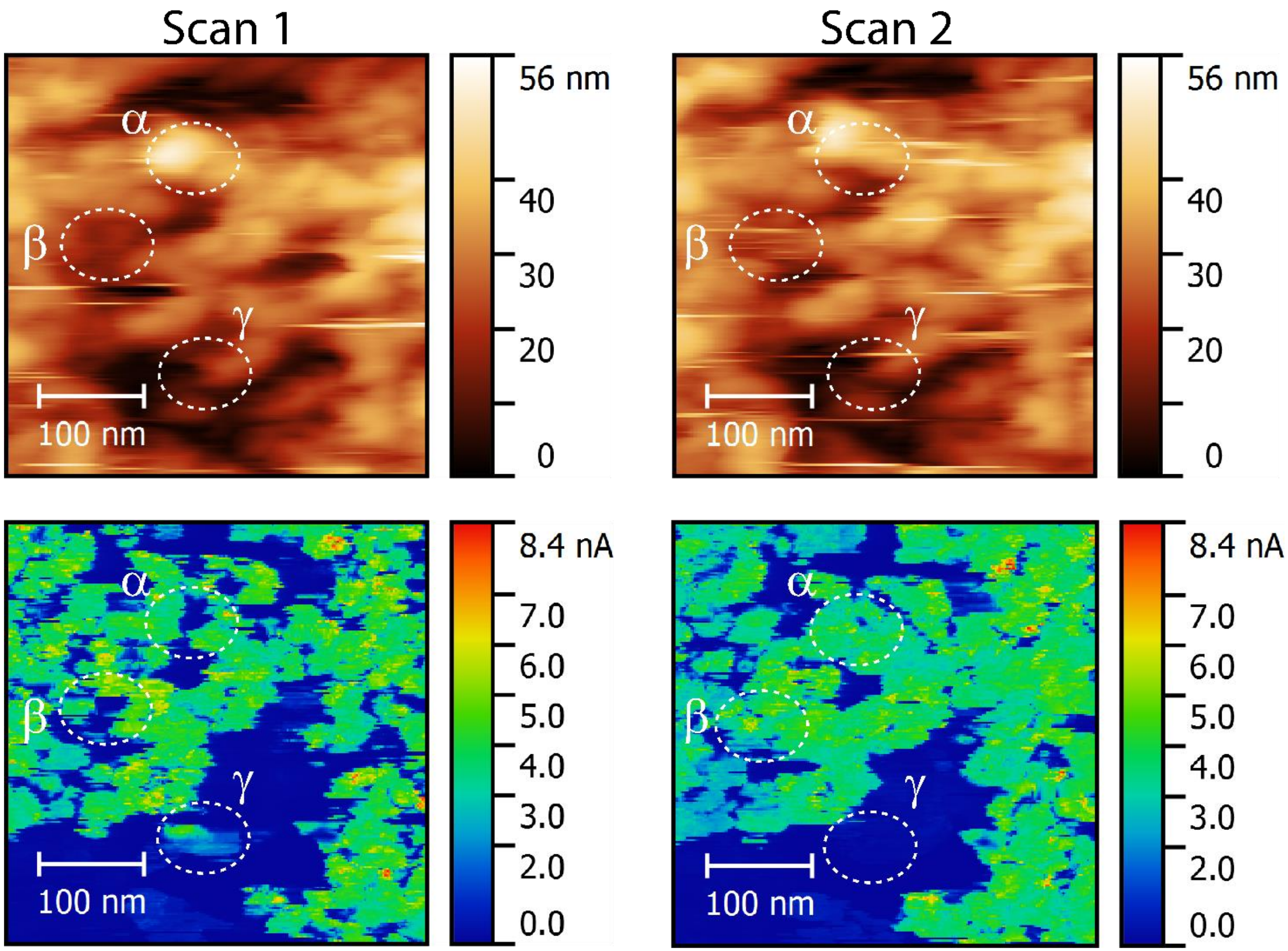
Chen, Q.; Guest, J.R.; Thimsen, E., Visualizing Current Flow at the Mesoscale in Disordered Assemblies of Touching Semiconductor Nanocrystals. *In Preparation.*

Subnetworks



Chen, Q.; Guest, J.R.; Thimsen, E., Visualizing Current Flow at the Mesoscale in Disordered Assemblies of Touching Semiconductor Nanocrystals. *In Preparation.*

Blinking (T=38K)



Chen, Q.; Guest, J.R.; Thimsen, E., Visualizing Current Flow at the Mesoscale in Disordered Assemblies of Touching Semiconductor Nanocrystals. *In Preparation.*

Conclusions from visualization

- The model of Skinner, Chen and Shklovskii is an excellent starting point for understanding charge transport in large numbers of nanocrystals that display an ES-VRH mechanism.
- We have observed **SUBNETWORKS** of uniformly higher resistance that appear to be connected to the conduction backbone by a tenuous high resistance link.
- The network displays dynamics that result in large regions both joining and disconnecting from the network.

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2) Institute for Materials Science and Engineering (IMSE) at WUStL
3) Center for Nanoscale Materials (ANL)

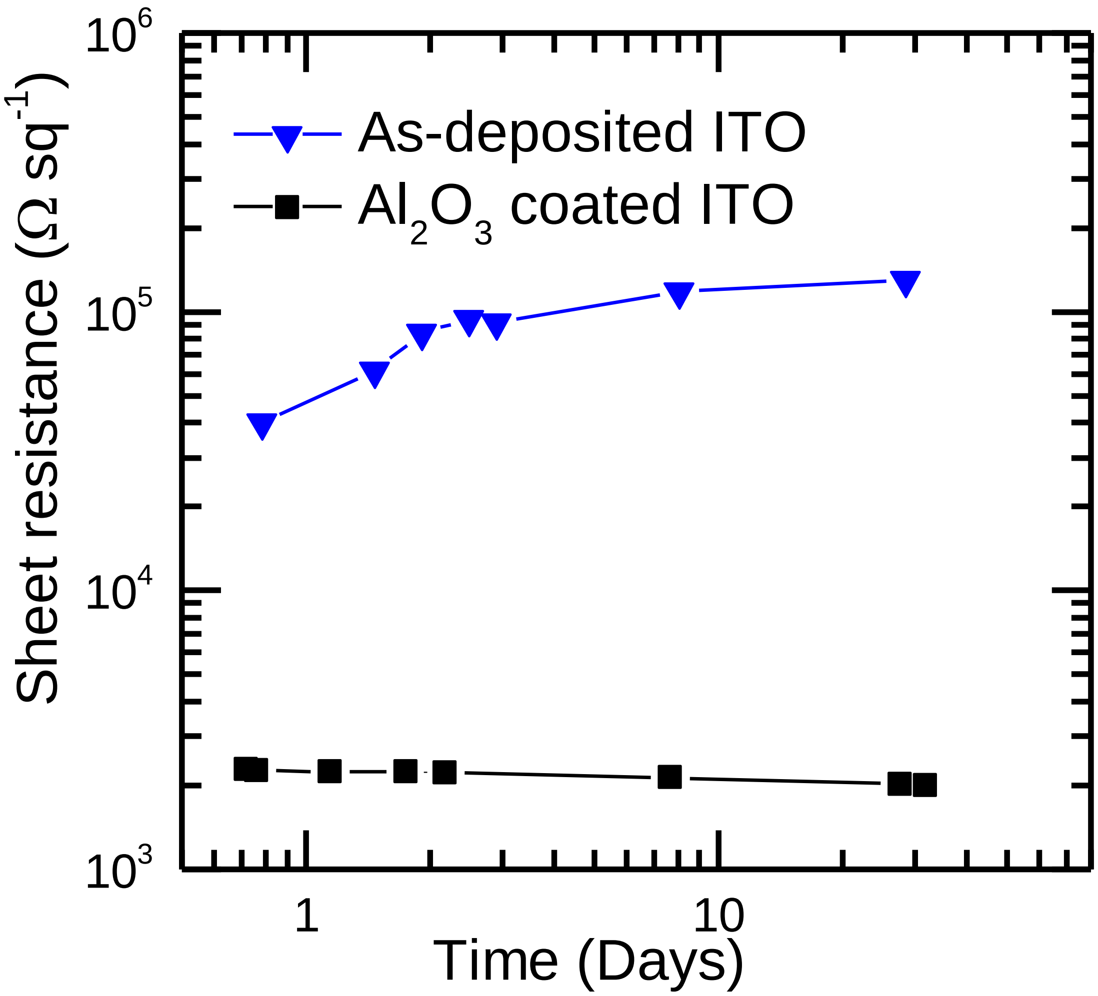
Interface Research Group

1) Deanna Lanigan
2) John Ephraim
3) Qinyi Chen

Collaborators

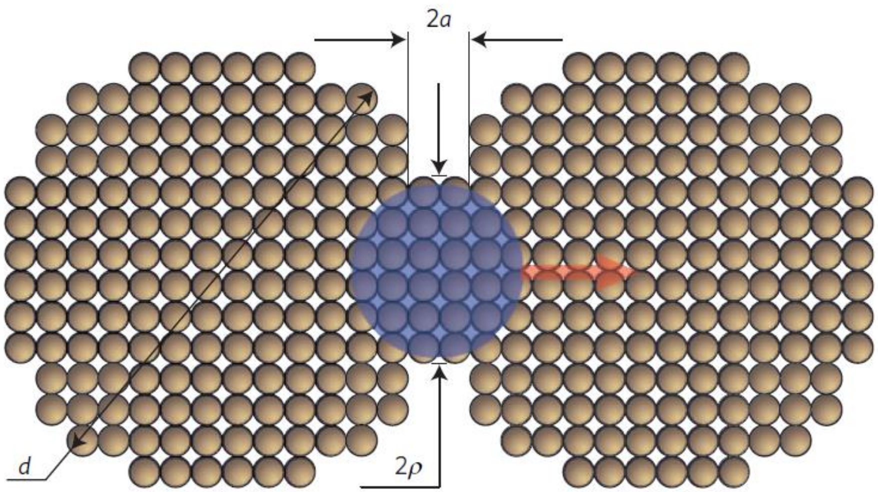
1) Jeffrey R. Guest (ANL)
2) Delia Milliron (UT Austin)
3) Corey Staller (UT Austin)

Also works for other materials…



Ephraim, J.; Lanigan, D.; Staller, C.; Milliron, D. J.; Thimsen, E. Transparent Conductive Oxide Nanocrystals Coated with Insulators by Atomic Layer Deposition. *Chem. Mater. 2016, 28, 5549-5553.*

IMT in arrays of touching nanocrystals



$$n_{crit} r_C^3 \approx 0.3g$$

Minimum values for r_C

Faceted contact: $r_C \approx \sqrt{r_0 a}$

Point contact: $r_C \approx \sqrt{r_0 b}$

If $n_{crit} r_C^3 << 0.3$

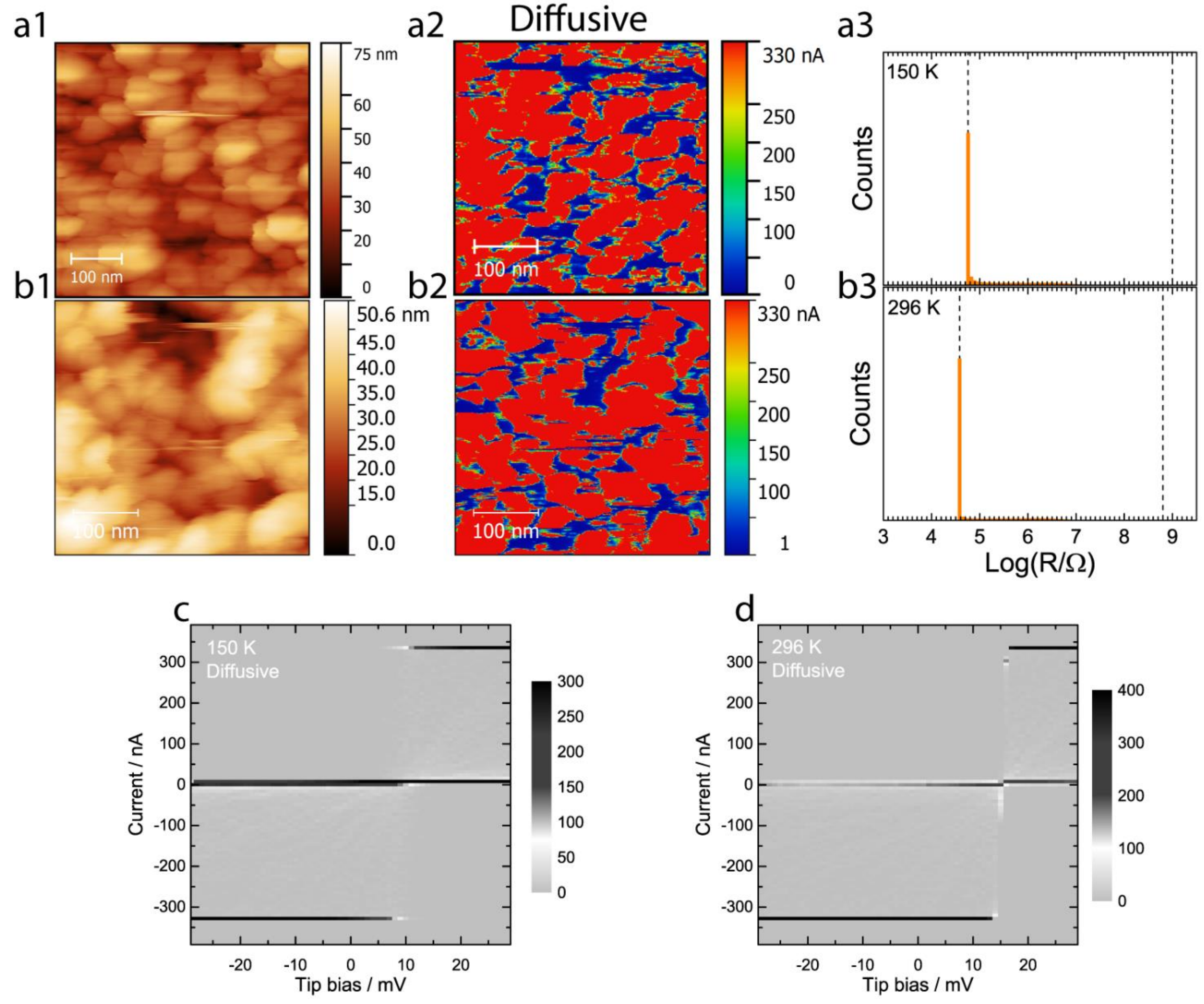
Then: $\rho(T) = \rho_0 \exp\left[\left(T_0/T\right)^m\right]$

If $n_{crit} r_C^3 >> 0.3$

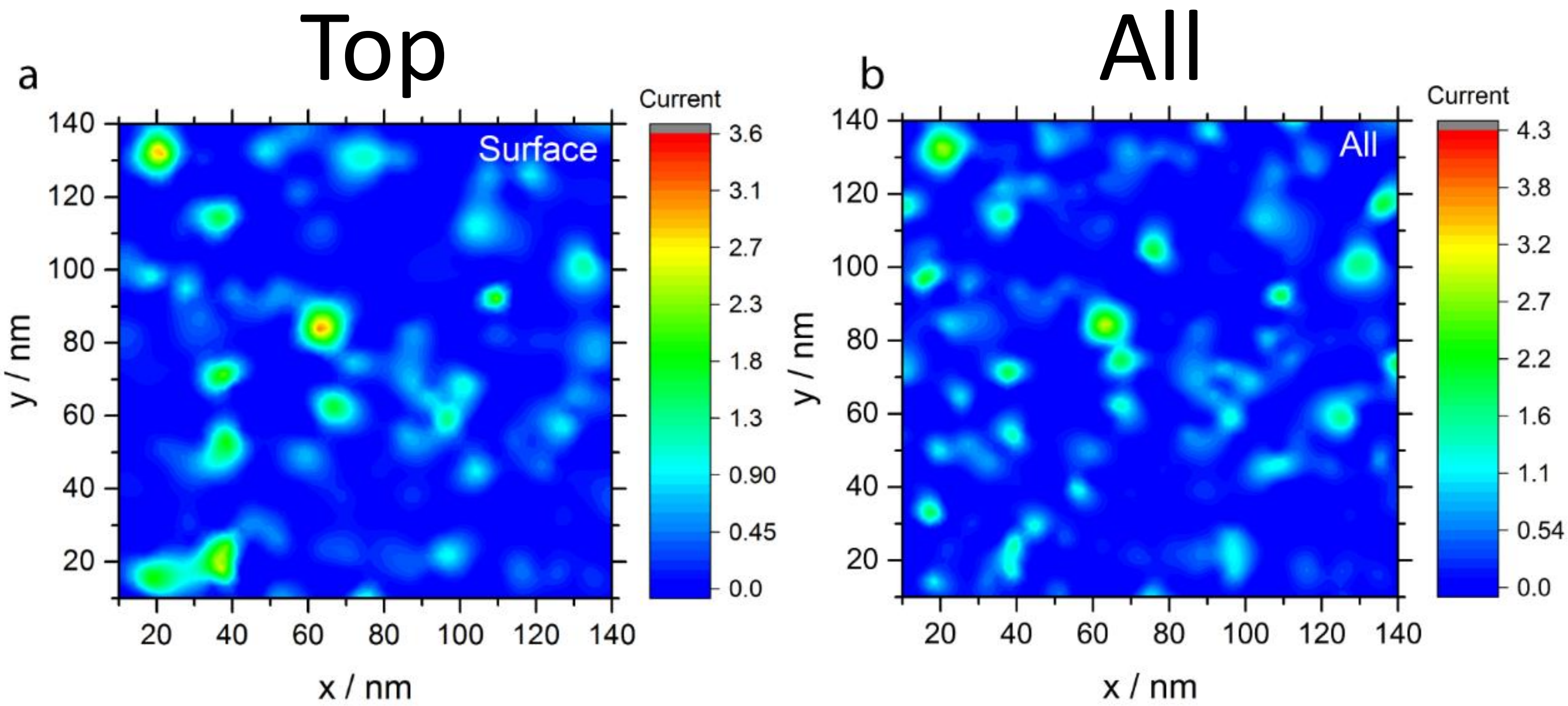
Then: $\rho(T) = \left[A + B\ln(T)\right]^{-1}$

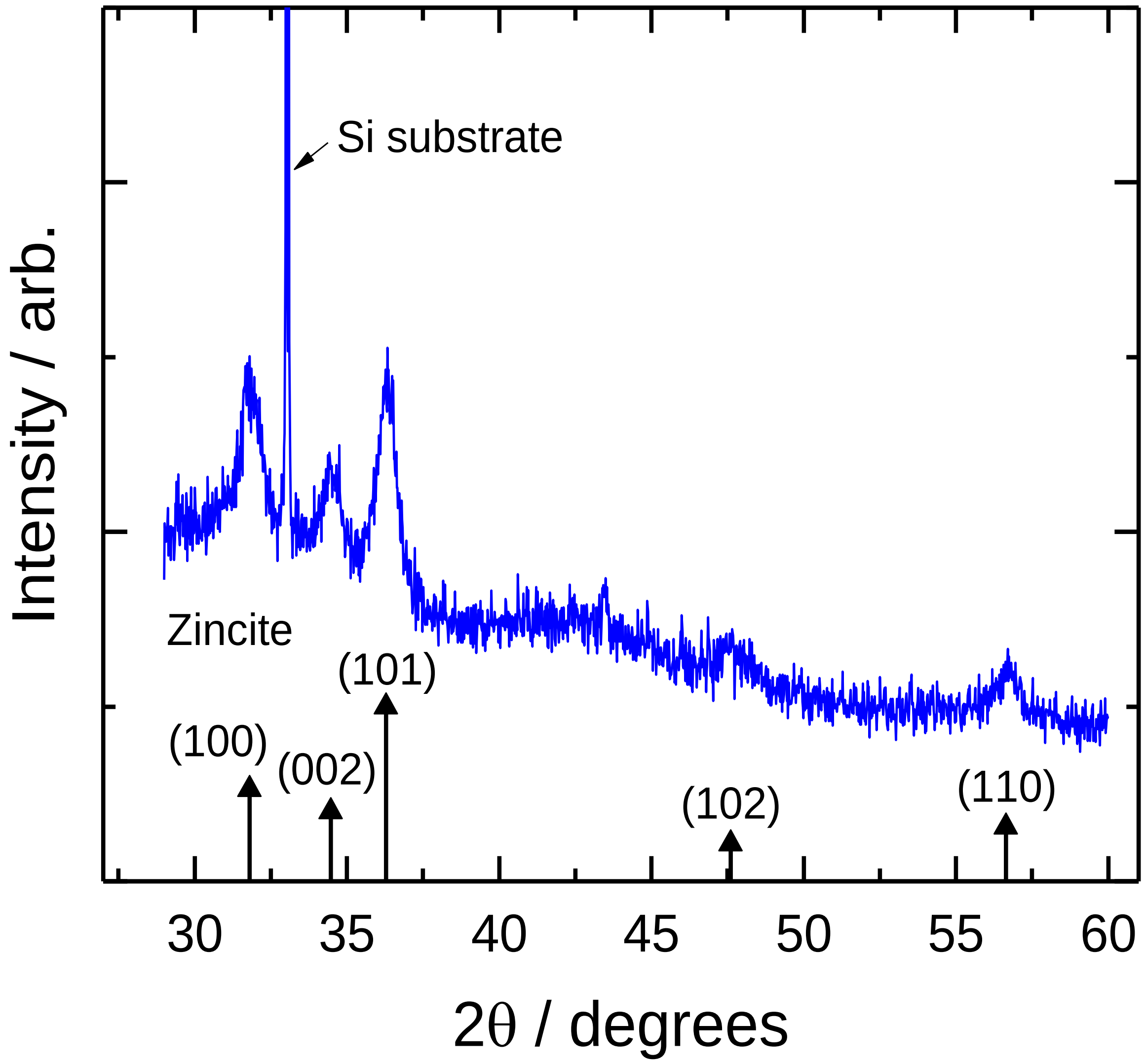
Chen, T.; Reich, K. V.; Kramer, N. J.; Fu, H.; Kortshagen, U. R.; Shklovskii, B. I., *Nat. Mater.* ***2016****, 15, (3), 299.*
Beloborodov, I. S.; Lopatin, A. V.; Vinokur, V. M.; Efetov, K. B.; *Rev. Mod. Phys.* ***2007****, 79, (2), 469-518.*

Diffusive sample

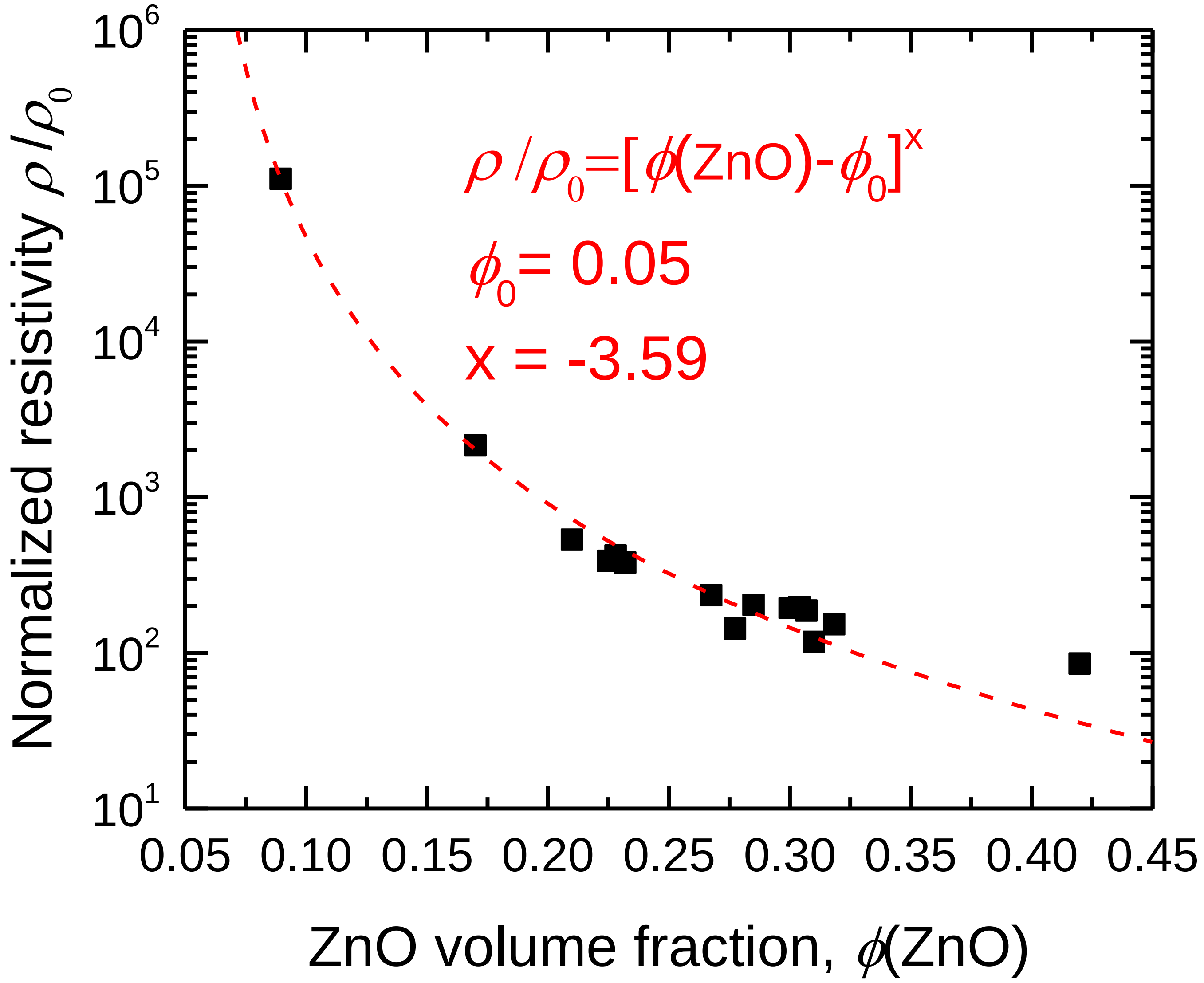


T=38 K

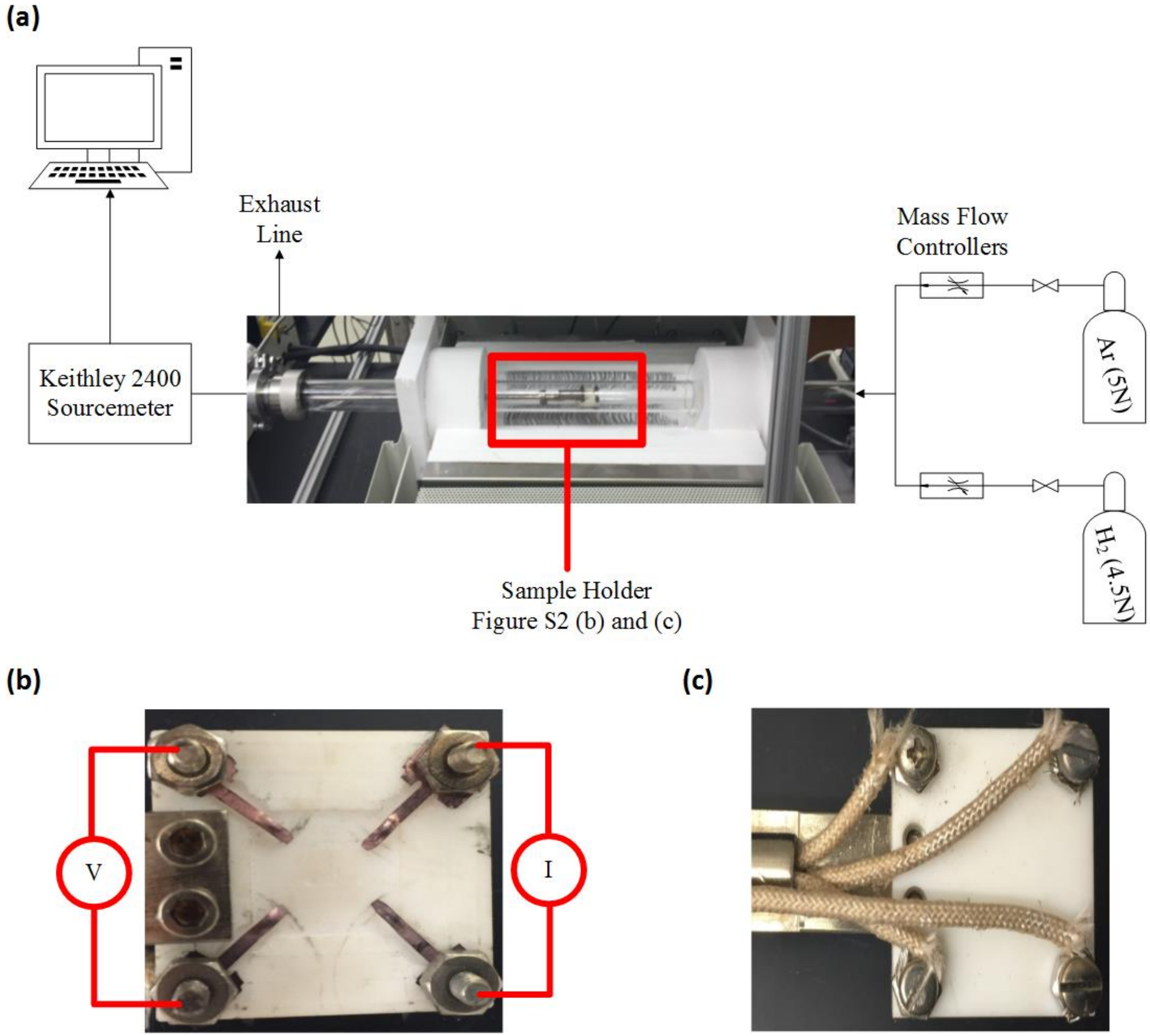

Top
All
a
b
Surface
All
Current
3.6
3.1
2.7
2.3
1.8
1.3
0.90
0.45
0.0
Current
4.3
3.8
3.2
2.7
2.2
1.6
1.1
0.54
0.0
y / nm
x / nm
140
120
100
80
60
40
20



Si substrate
Intensity / arb.
Zincite
(101)
(100)
(002)
(102)
(110)
30
35
40
45
50
55
60
2θ / degrees



Normalized resistivity ρ/ρ0
10^6
10^5
10^4
10^3
10^2
10^1
0.05 0.10 0.15 0.20 0.25 0.30 0.35 0.40 0.45
ZnO volume fraction, ϕ(ZnO)
ρ/ρ0=[ϕ(ZnO)-ϕ0]^x
ϕ0= 0.05
x = -3.59



(a)
Exhaust
Line
Mass Flow
Controllers
Keithley 2400
Sourcemeter
Ar (5N)
H2 (4.5N)
Sample Holder
Figure S2 (b) and (c)
(b)
V
I
(c)