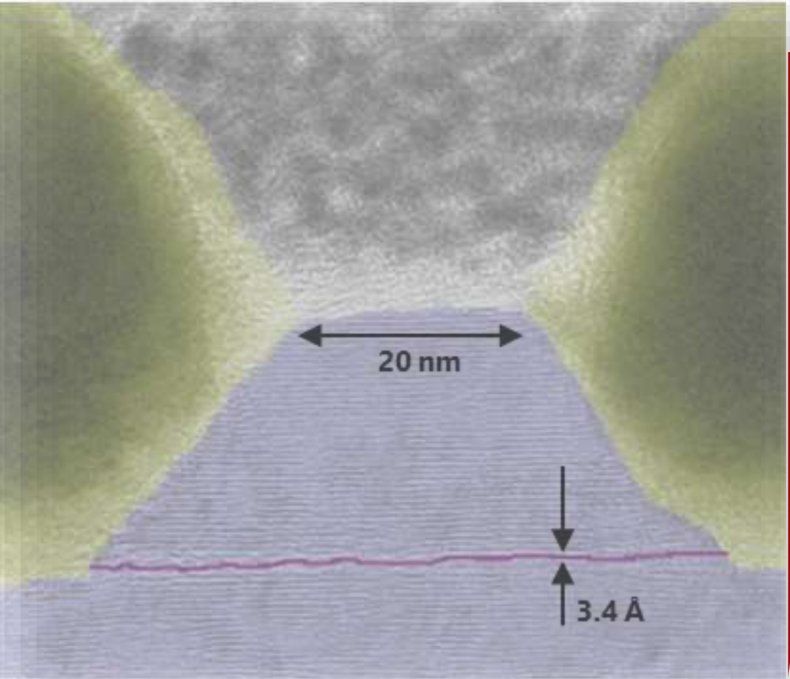
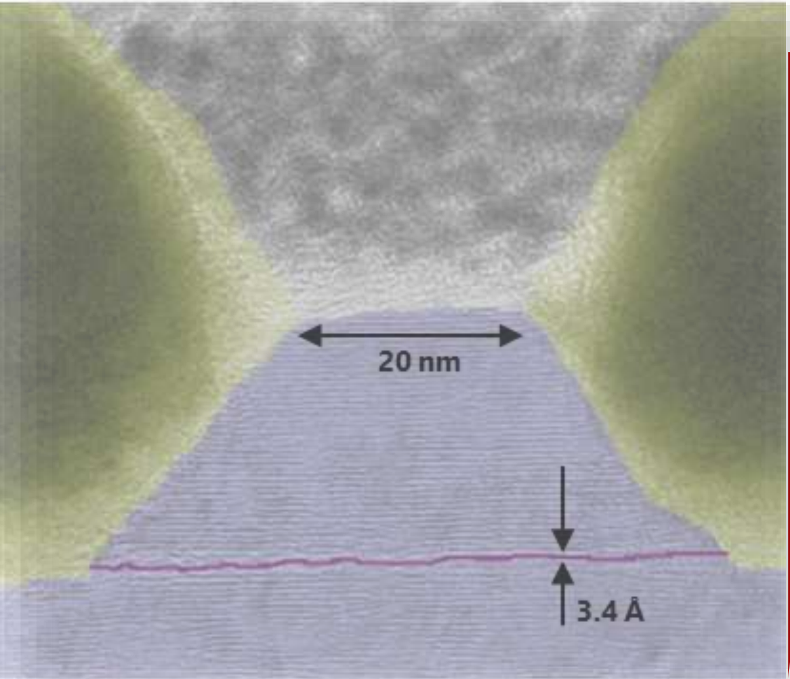


Integrating Low Dimensional Materials for Quantum Technology and Sensing

Michel Calame
Transport at Nanoscale Interfaces Laboratory, Empa, Switzerland
& Department of Physics, University of Basel, CH, Switzerland

www.empa.ch/tnilab

Quantum Workshop | 15-18 January 2024 | SNOLAB, Sudbury, CA



Integrating Low Dimensional Materials for Quantum Technology and Sensing

Outline

- Transistors from nanocarbons: charge & current
- Photodetectors from colloidal qdots
- Upscaling (?)

Quantum Workshop | 15-18 January 2024 | SNOLAB, Sudbury, CA

ETH Domain in Switzerland

% = share of base funding

ETH Domain in Switzerland - Empa

Materials & technologies for a sustainable future

% = share of base funding

Research Focus Areas at Empa

Nanoscale Materials & Technologies

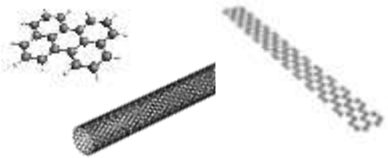
Built Environment

Health & Performance

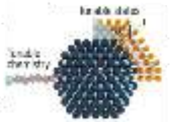
Energy, Resources & Emissions

Integrating Low Dimensional Materials for Quantum Technology and Sensing

Nanocarbons

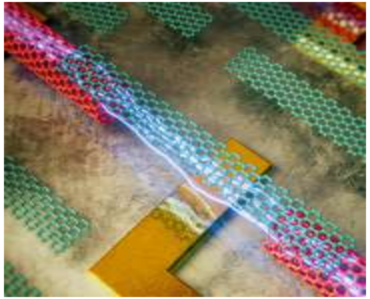


Synthetic Qdots



de Arquer *et al.* Science (2021)

Devices

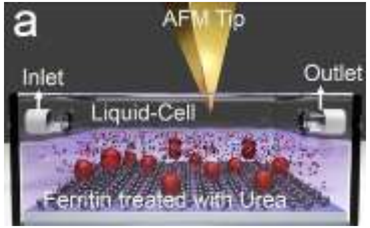


Molecules & Biomarkers

2D materials

Novoselov *et al.* Science (2016)

Methods



Integrating Low Dimensional Materials for Quantum Technology and Sensing

The promise(s) of low-dimensional materials

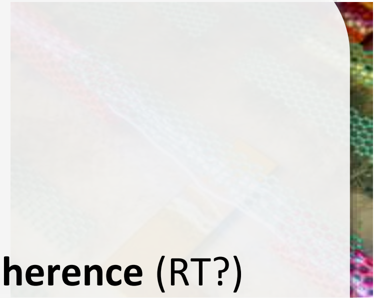
- **Unique** physical and (opto-)electronic **properties (meV-eV); coherence** (RT?)
- **Ultra-thin channel**: high-speed, low power (opto-)electronics
- Highly **crystalline** (controlled doping/defects: each atom matters)
- **Low-temperature processing**: 3D integration of multiple active device layers
- Improved **thermal management**

Nanocarbons

Synthesis

de Arquer *et al.* Science (2021)

Devices



Molecules & Biomarkers

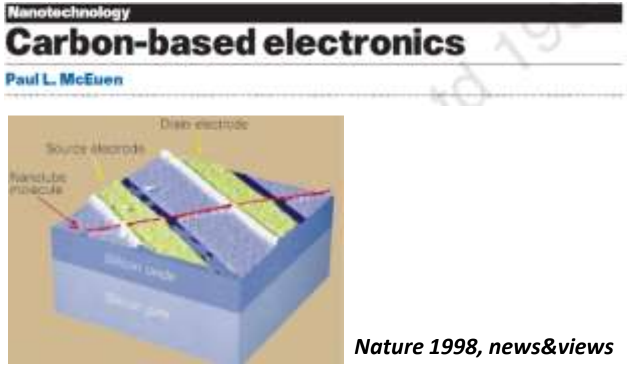
2D materials

Novoselov *et al.* Science (2016)

Methods

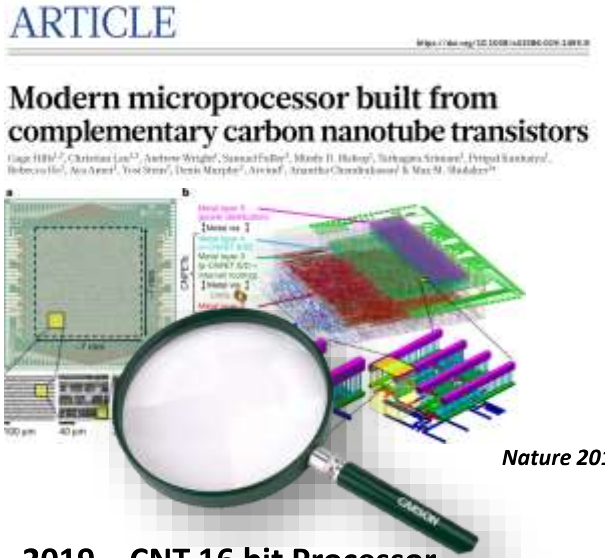
A long-standing promise

Are we there yet ?



Nature 1998, news&views

1998 – Research Devices, CNT Transistor

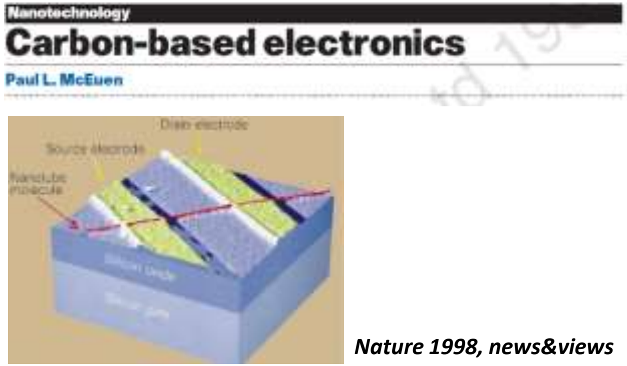


Nature 2019

2019 – CNT 16 bit Processor

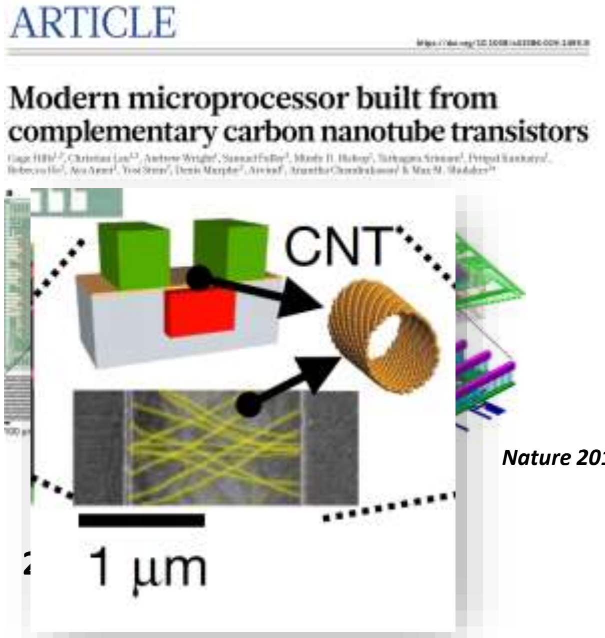
A long-standing promise

Are we there yet ?



Nature 1998, news&views

1998 – Research Devices, CNT Transistor



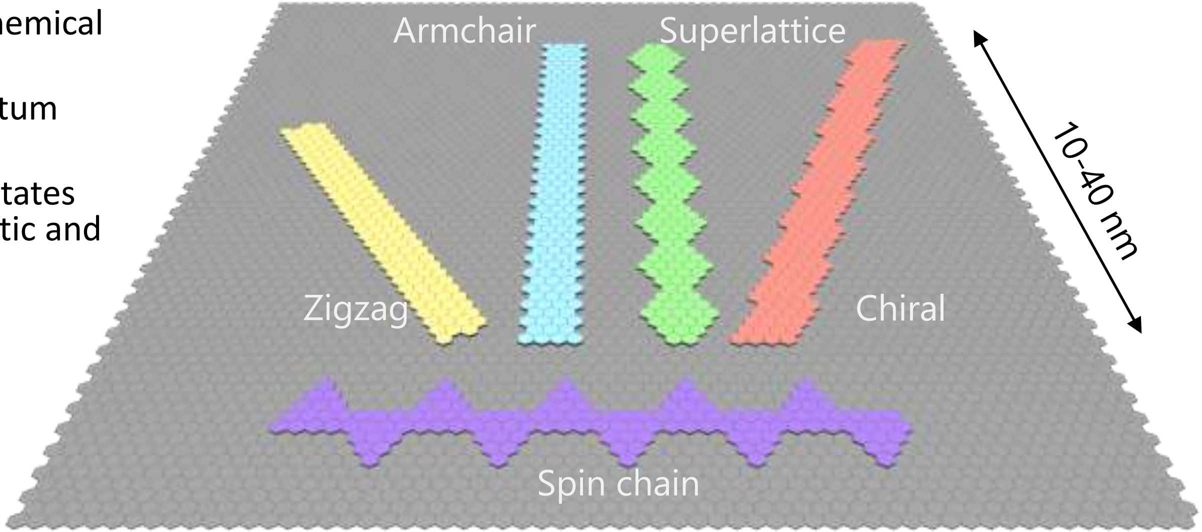
Nature 2019

Still, not individual Carbon Nanotubes …

An emerging Material: Graphene Nanoribbons

Advantages

- Bottom-up synthesized
- Largely tunable chemical structure
- Pronounced quantum effects
- Edge structure dictates electronic, magnetic and optical properties



In collaboration with Prof. R. Fasel

Dr. G. Borin Barin

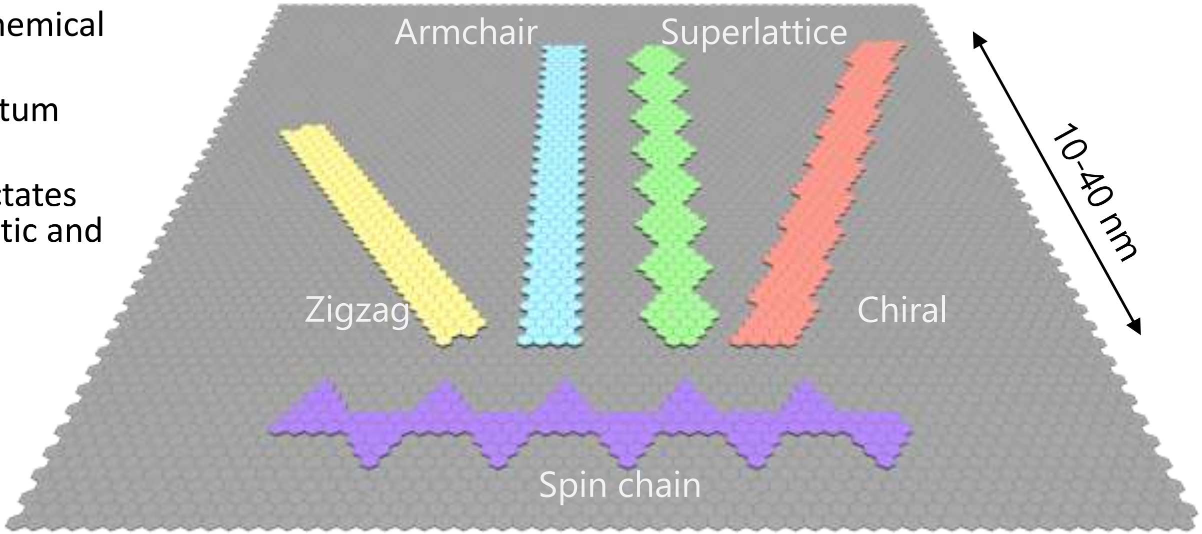
with Prof. Mickael Perrin

An emerging Material: Graphene Nanoribbons

ZZ: metallic (n.n. tight-binding); edges: ferromag. ordering (channels near Fermi); spintronics
AC: metallic or semiconducting (width) – cf nanotubes
SL: top. Protected spin centers, tunable exchange interaction

Advantages

- Bottom-up synthesized
- Largely tunable chemical structure
- Pronounced quantum effects
- Edge structure dictates electronic, magnetic and optical properties



In collaboration with Prof. R. Fasel

Dr. G. Borin Barin

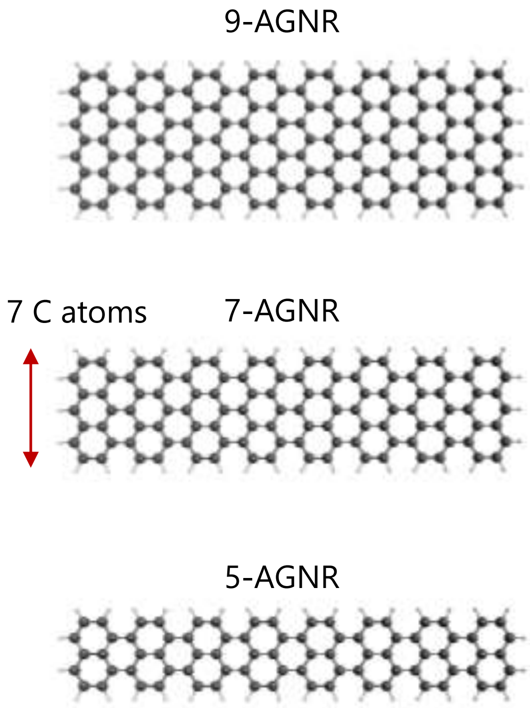
Highly-tunable and fully carbon-based material class

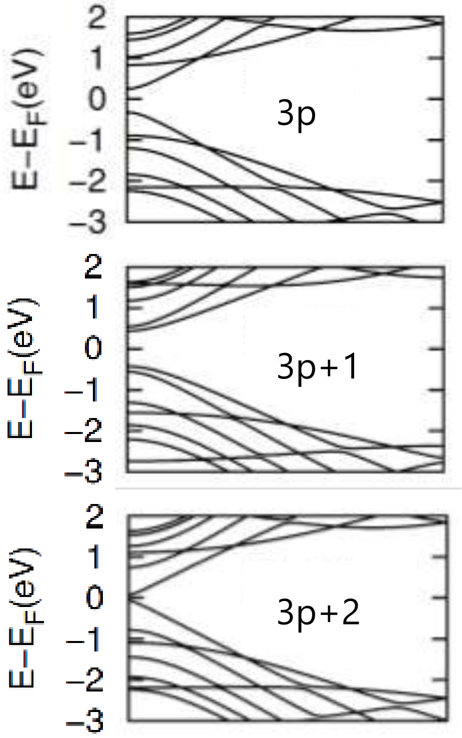
NB: stability/encapsulation

Graphene Nanoribbons: Tunable Properties

Armchair GNRs (AGNRs)

$$E_g \sim \frac{1}{w_{GNR}}$$





medium bandgap

wide bandgap

low bandgap quasi-metallic

Finite size leads to bandgap and edge states

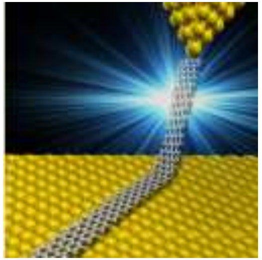
M..S. Dresselhaus et al., Phys. Rev. B (1996)

M. Sigrist et al., Phys. Rev. B (1999)

S.G. Louie, M. Cohen et al., Phys. Rev. Lett. (2006, 2007)

Contacting GNRs

STM approach
UHV, 4K

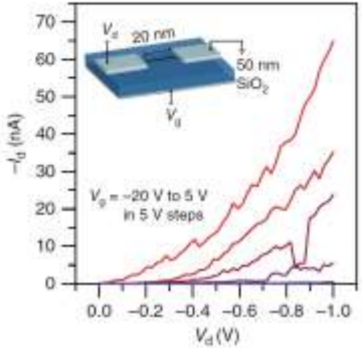


G. Schull et al., Nano Lett. (2017)

Magnetic porphyrin bonded to GNRs
J.I. Pascual et al., Sci. Adv. (2018)

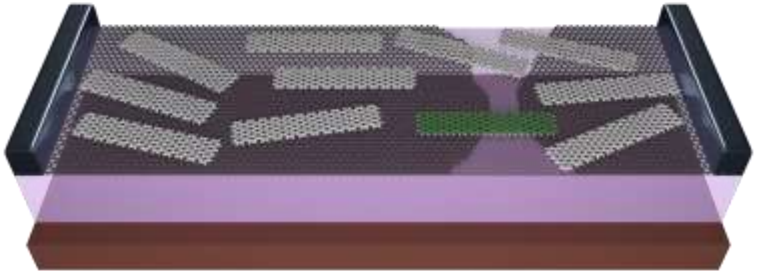
Device geometry
Ambient, room temp.

9- & 13AGNRs, wide bandgap, **metallic contacts (Pd)**
J. Bokor et al., Nat. Comm. (2017)



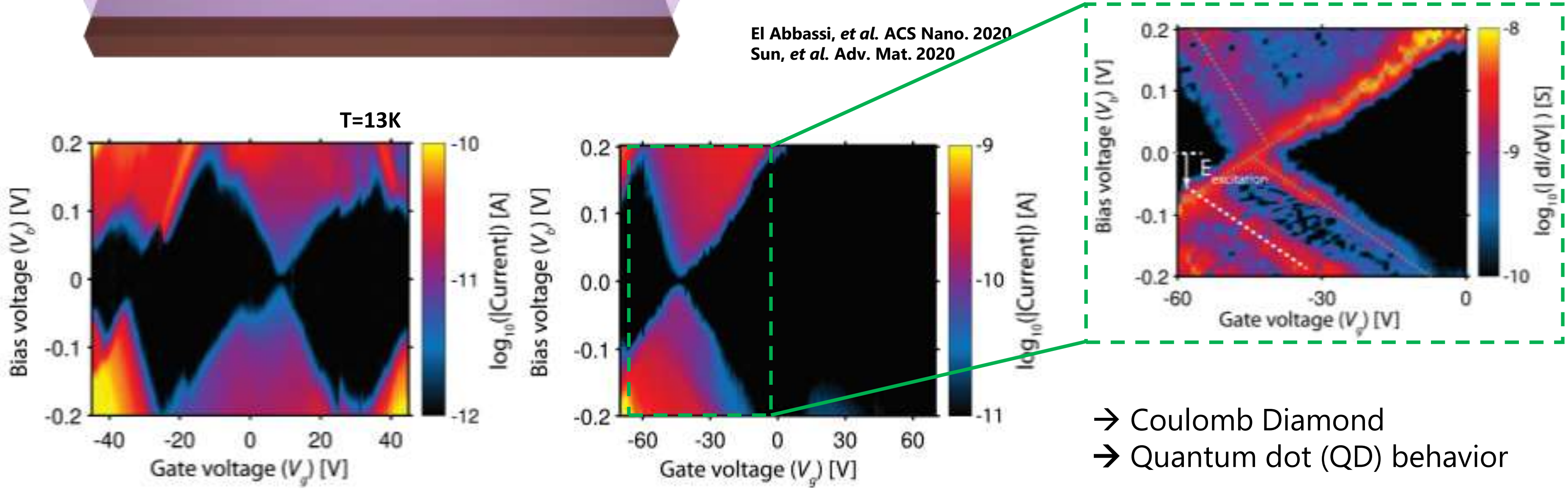
Issues
- GNRs size & positioning
- Contact control
- Correlation structure - transport

Graphene electrodes & First Devices



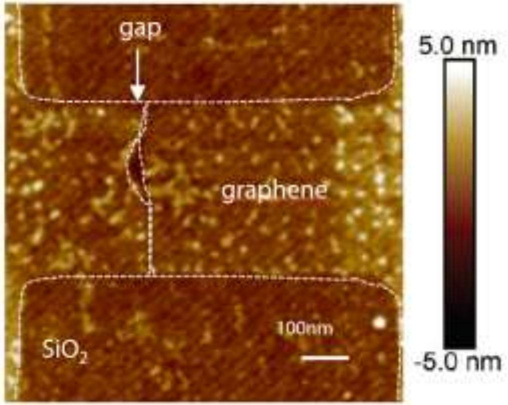
Nanogap size : ~ 1-5 nm

El Abbassi, *et al.* ACS Nano. 2020
Sun, *et al.* Adv. Mat. 2020

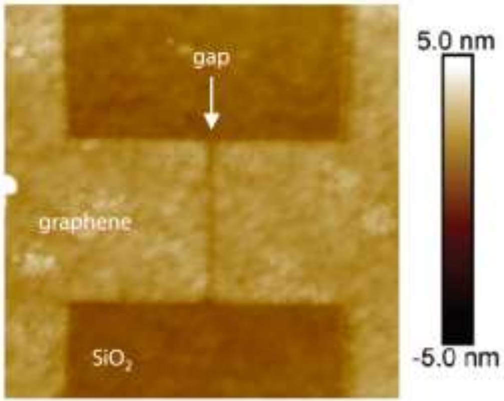


→ Coulomb Diamond
→ Quantum dot (QD) behavior

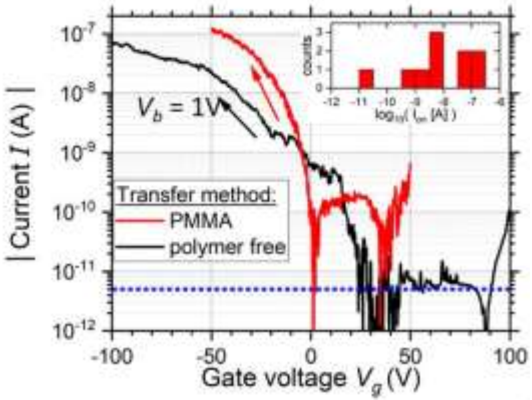
Improved Graphene Electrodes



El Abbassi, *et al.* Nat. Nano. 2019

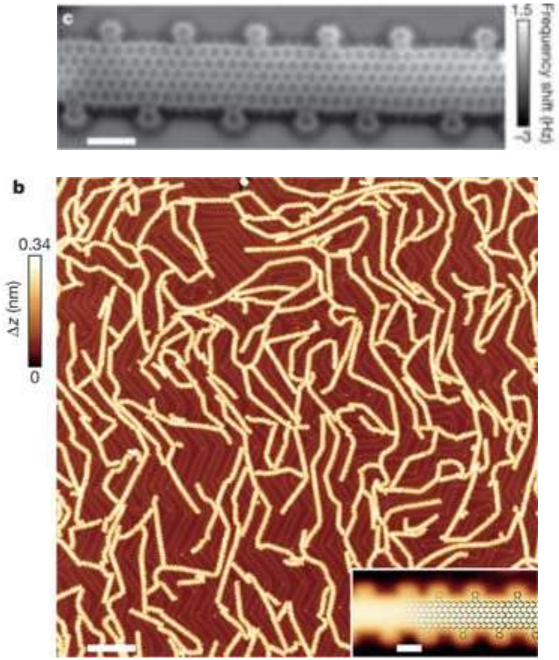


Braun, *et al.* Carbon 2021



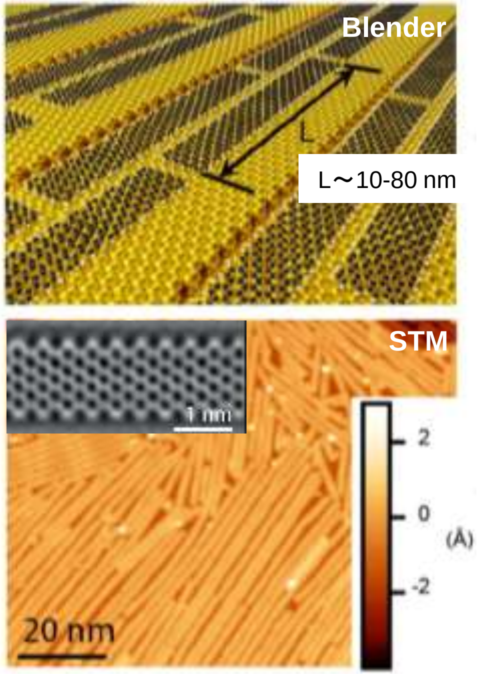
FET behavior with on/off currents ratio up to 10^4 at room temperature

GNRs orientation and ordering



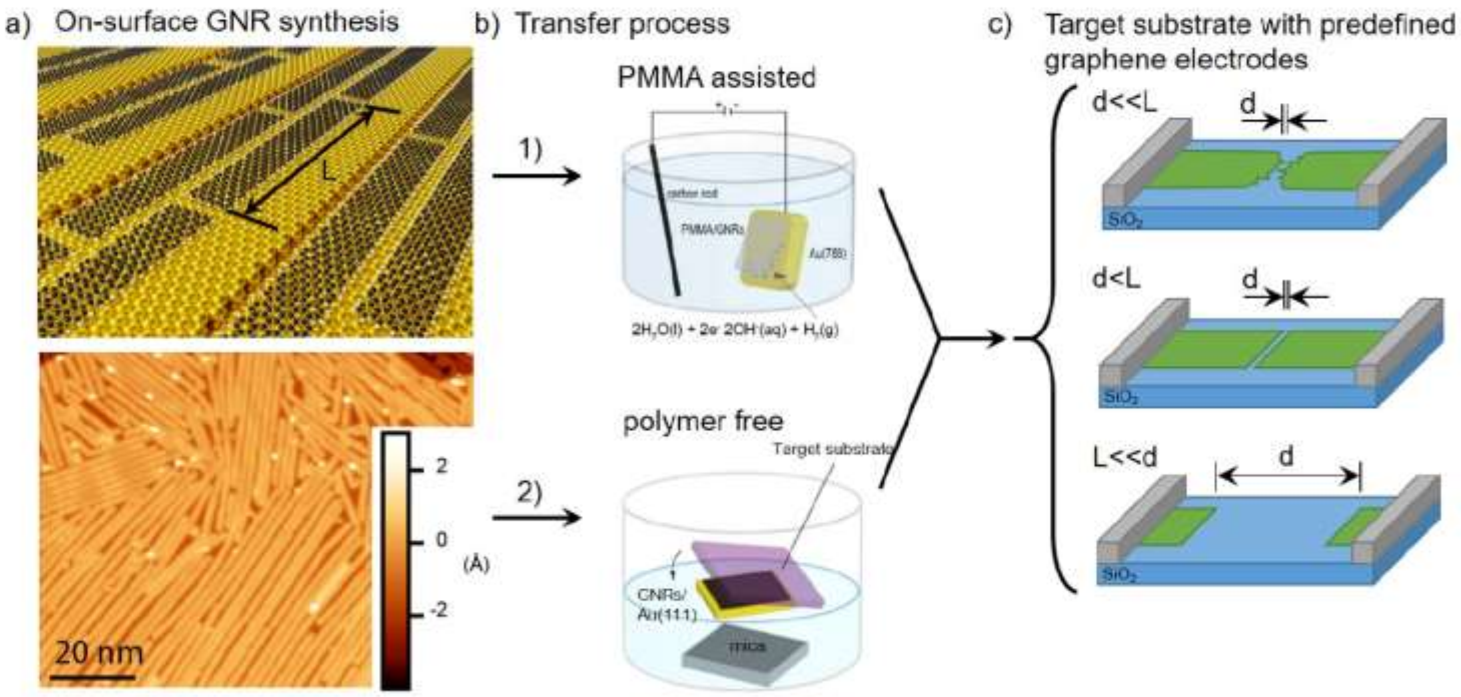
P. Ruffieux et al., Nature 531 (7595), 489 (2016)

Uniaxially **aligned** 9-AGNRs with a medium dense coverage on Au(788)



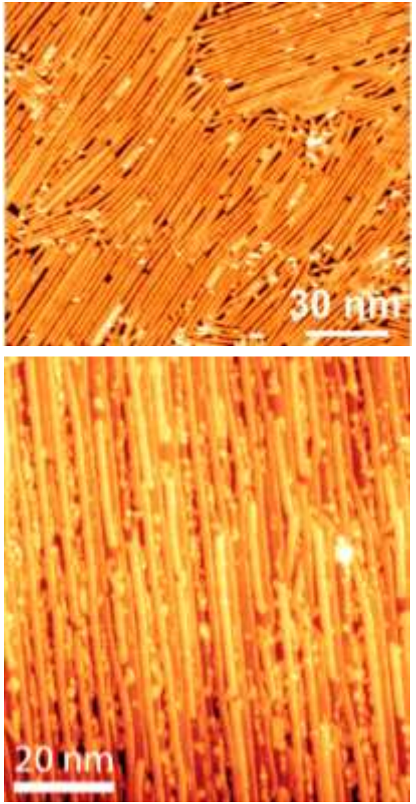
Borin Barin et al. ACS Appl. Nano Mater. (2019)

Graphene electrodes & GNRs transfer



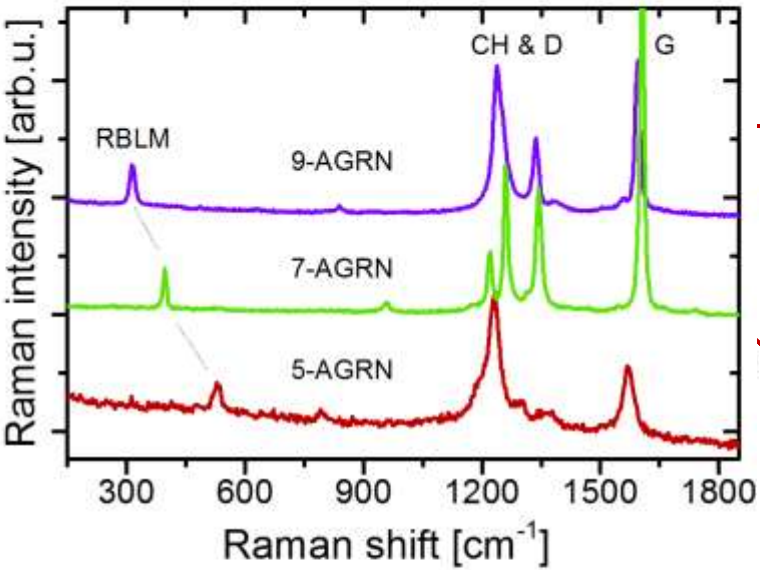
Borin Barin et al. *ACS Appl. Nano Mater.* (2019)
Overbeck,et al. *phys. stat. sol. (b)* (2019)
O. Braun, PhD Thesis (2021)

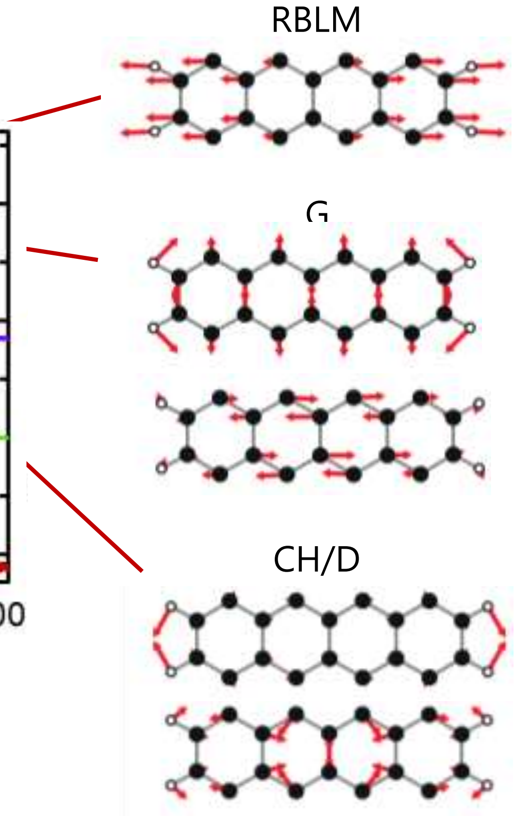
Raman Spectroscopy of GNRs



M. Di Giovannantonio et al., ACS nano 2018

Fingerprinting the type of GNR

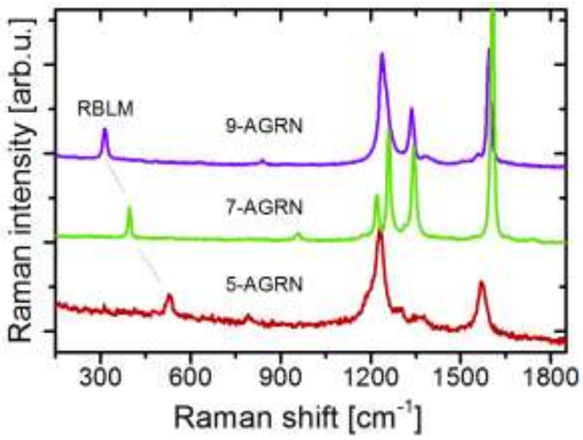




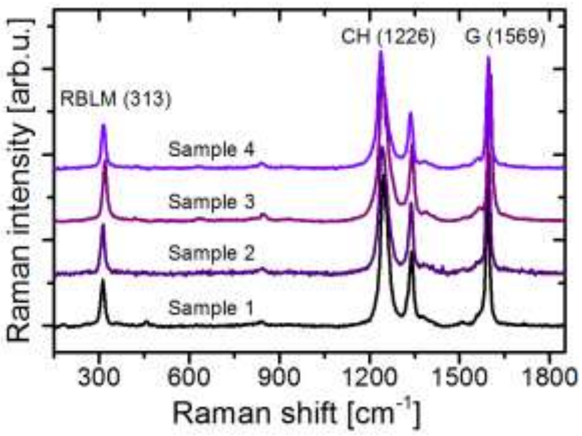
Overbeck, Perrin, *et al.* ACS nano 2019

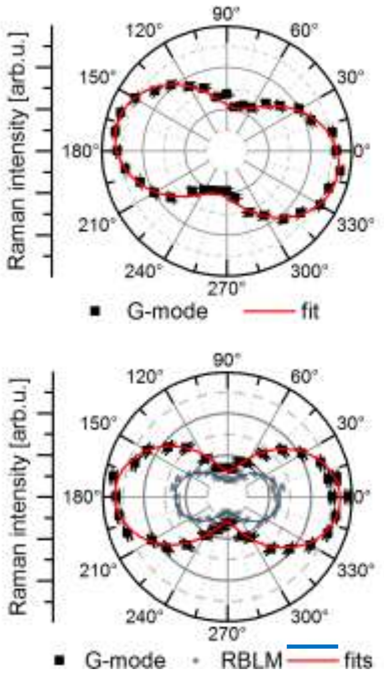
Raman Spectroscopy of GNRs

Fingerprinting the type of GNR



Assessing sample-to-sample variation



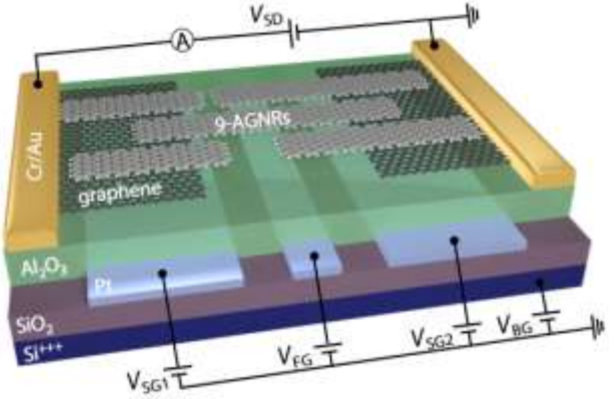


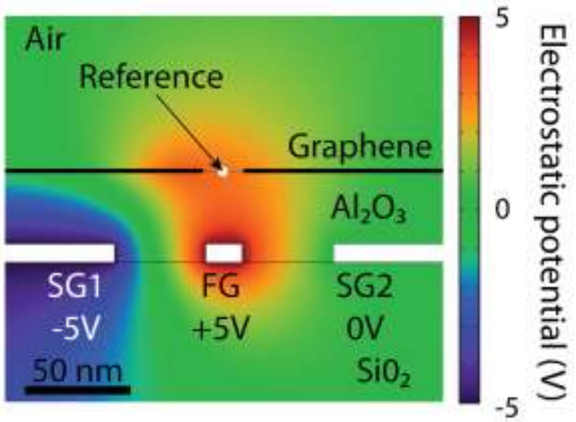
On growth substrate…

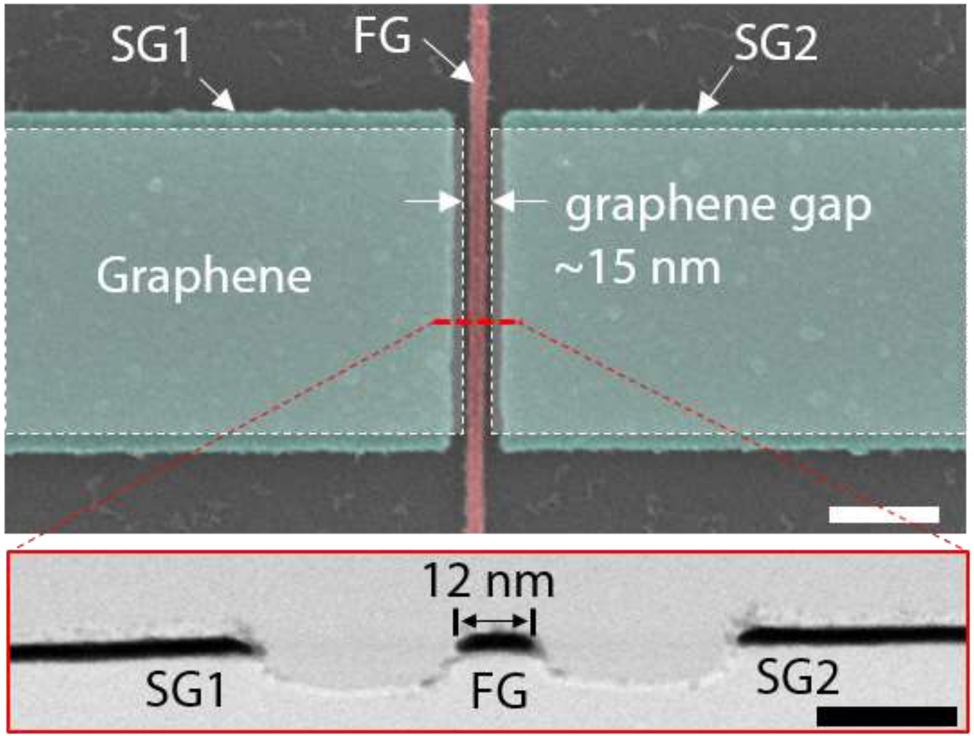
On device substrate…

Jan Overbeck et al. Pssb (2019); ACS Nano (2019)

Local Gates for Electrostatic Control



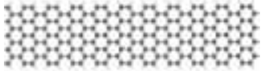


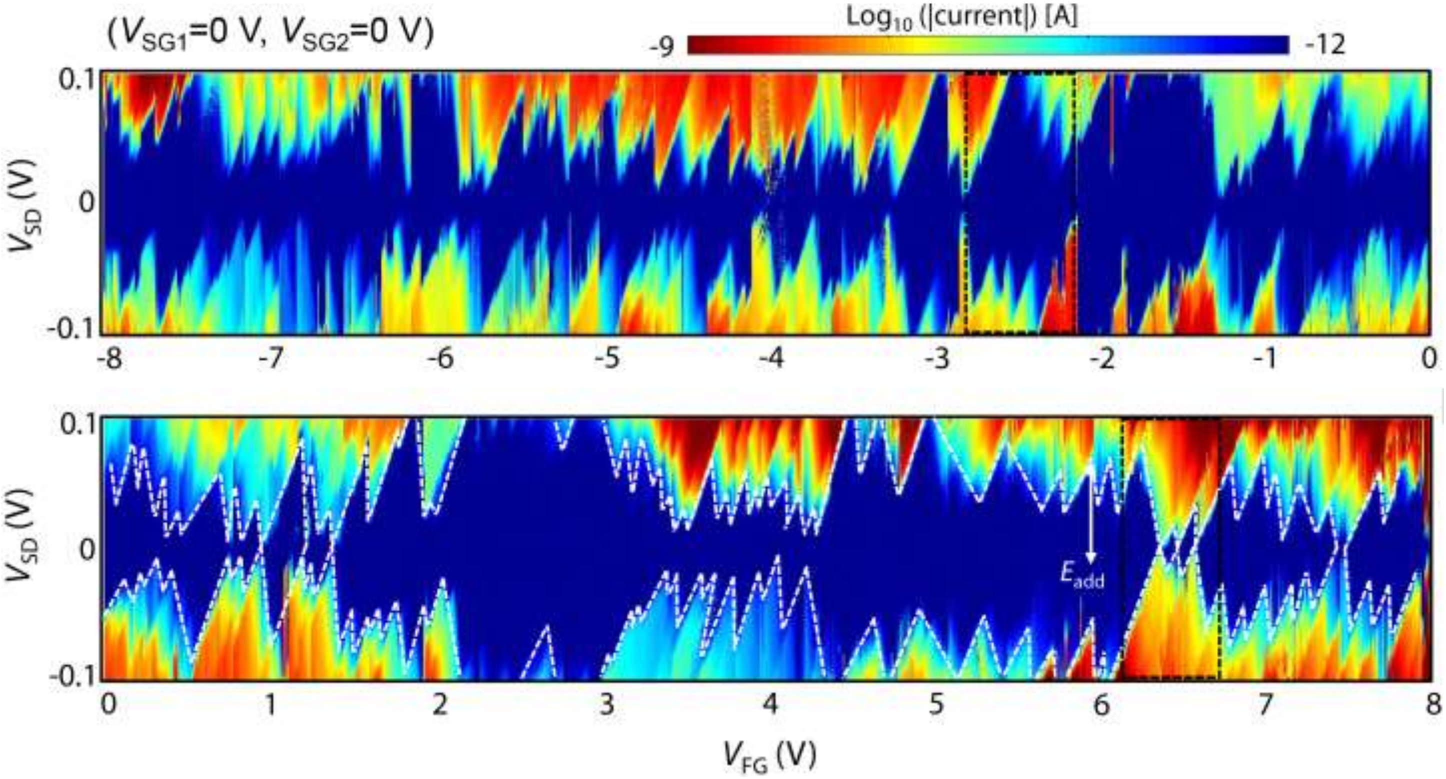


Zhang et al. Adv. Elect. Mat. 2023

Local Gates for Electrostatic Control

9-AGNRs





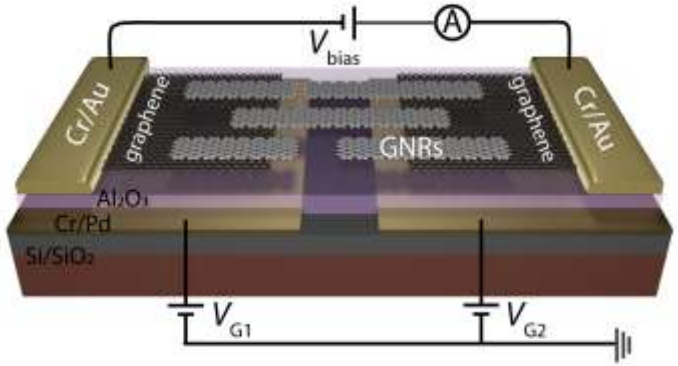
High gate coupling

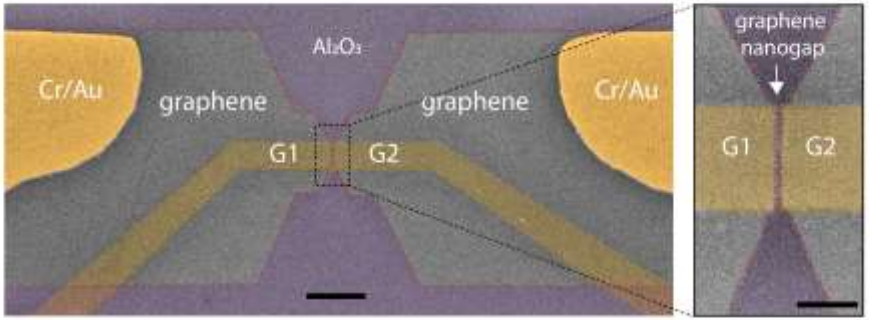
Many (overlapping) Coulomb diamonds

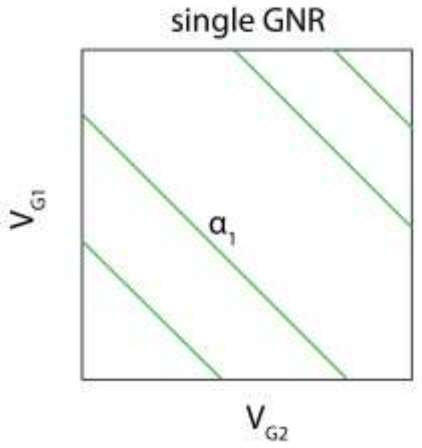
Complex structures

Zhang et al. Adv. Elect. Mat. 2023

… and for identifying the number of GNRs

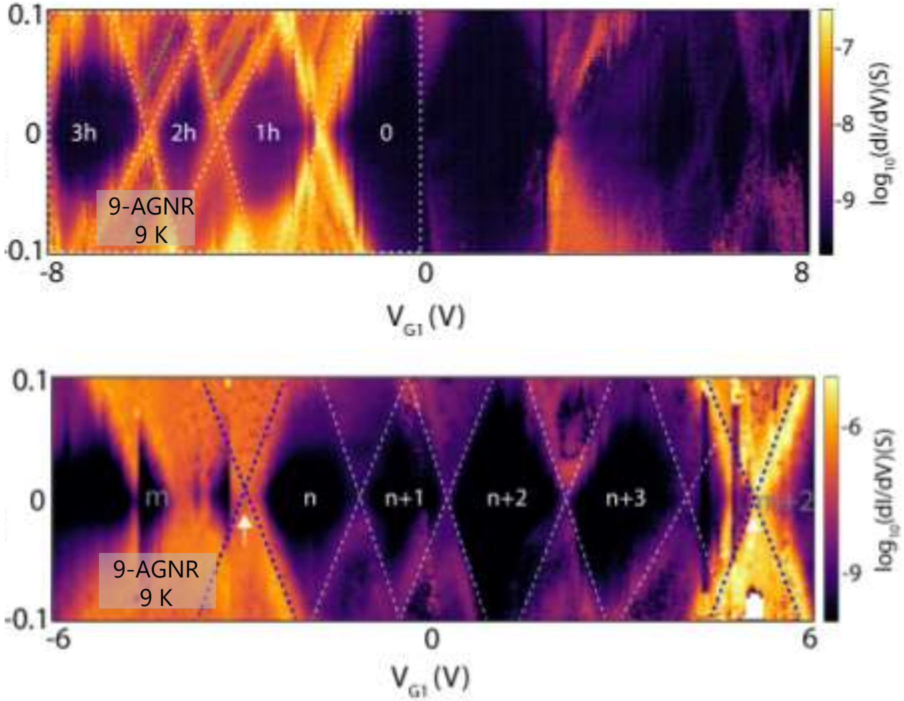






Zhang et al. Nano Letters, 2023

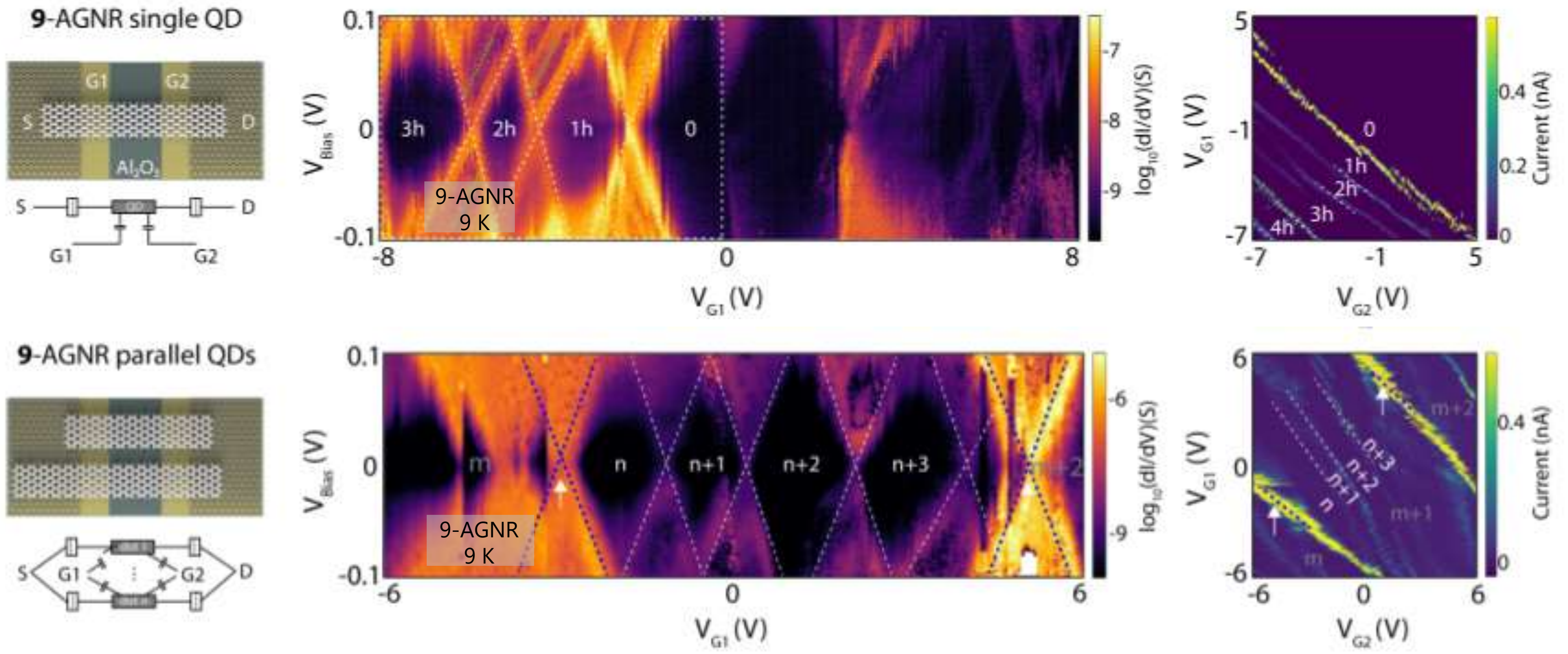
… and for identifying the number of GNRs



- Stability diagrams show well-defined Coulomb diamonds

Zhang et al. Nano Letters, 2023

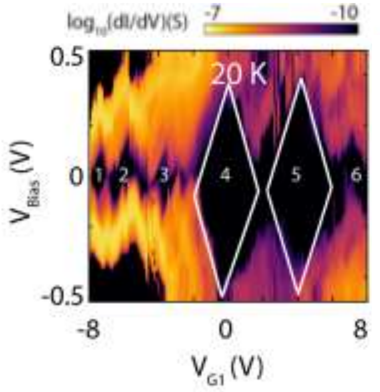
… and for identifying the number of GNRs

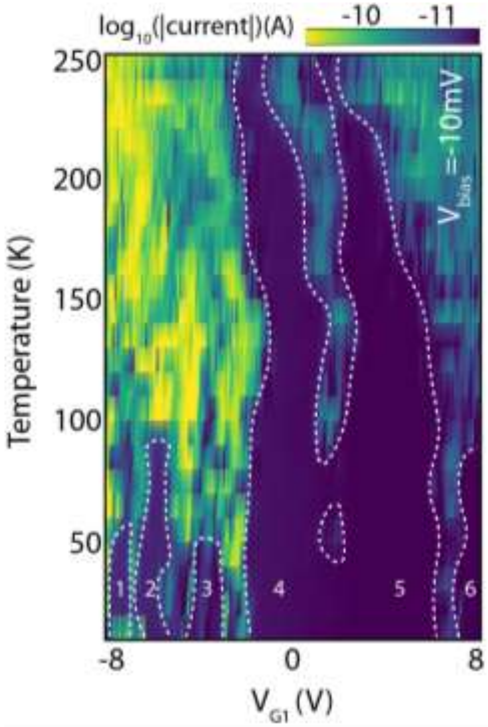


- Stability diagrams show well-defined Coulomb diamonds
- Gate-gate sweep helps identify the number of quantum dots

Zhang et al. Nano Letters, 2023

Temperature dependence of CB signature

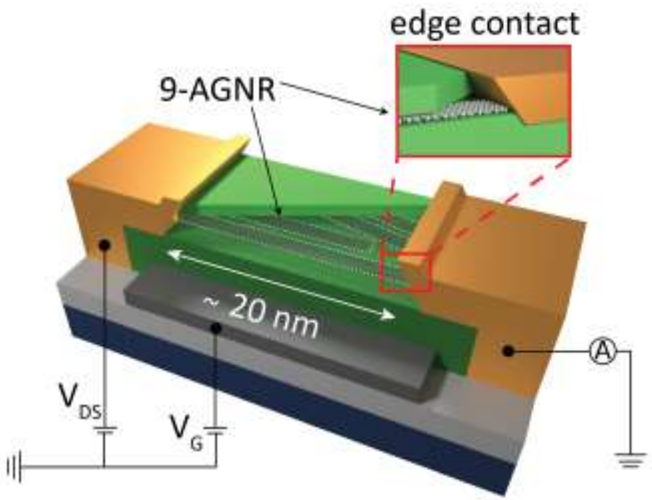


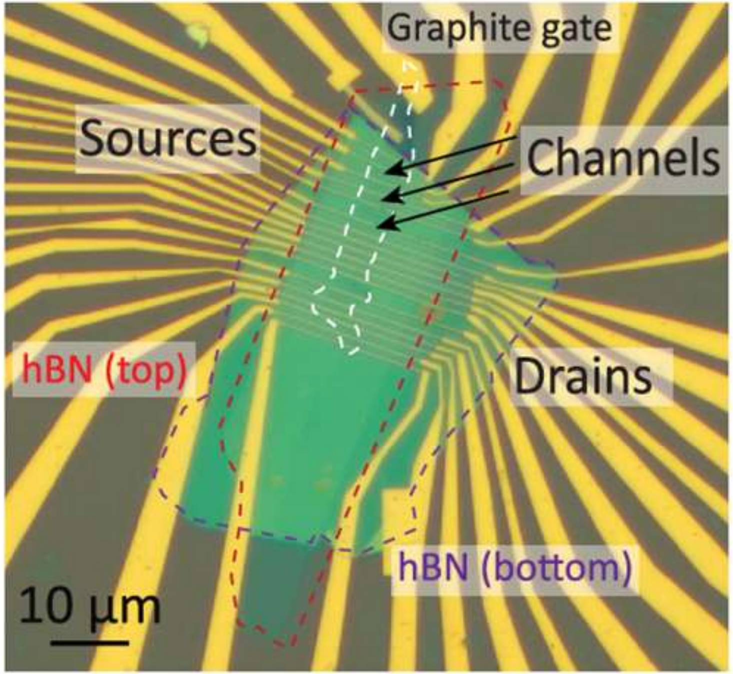


- Coulomb Blockade signature up to 250K

Zhang et al. Nano Letters, 2023

More on Contacts and Environment
Passivation and Edge Contacts

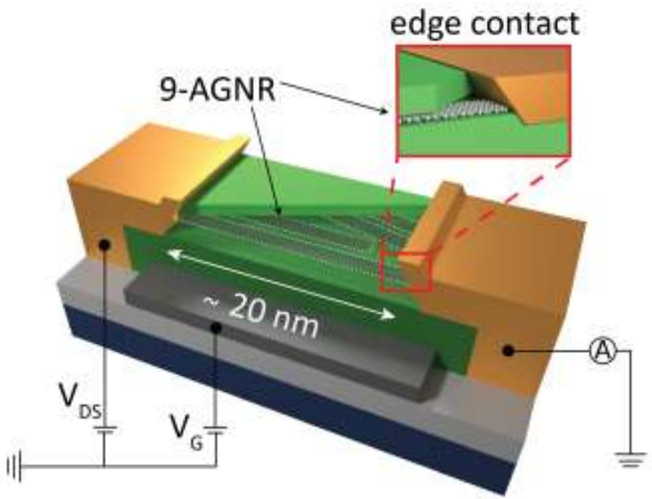




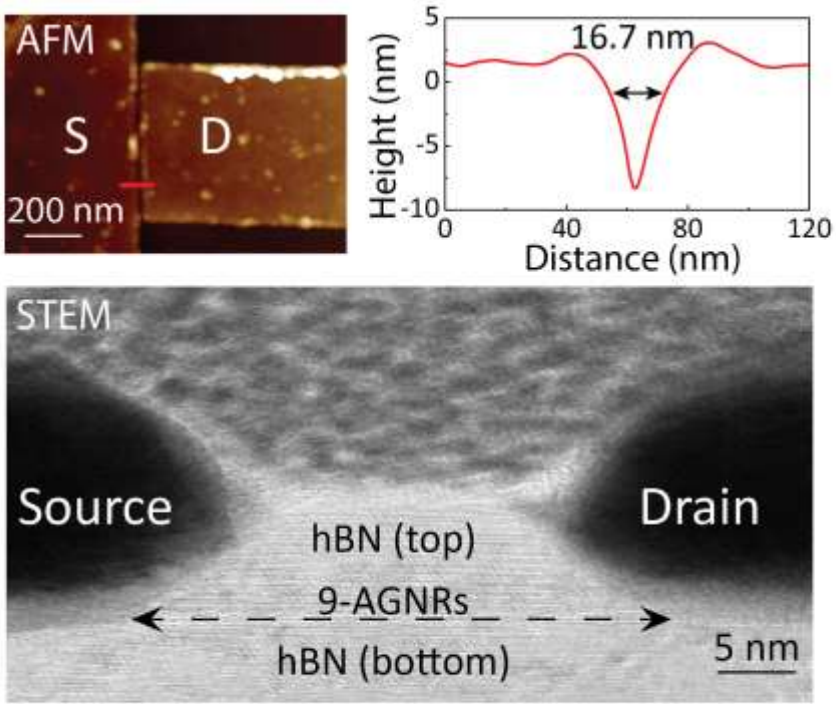
Huang et al. ACS Nano, 2023

More on Contacts and Environment

Passivation and Edge Contacts



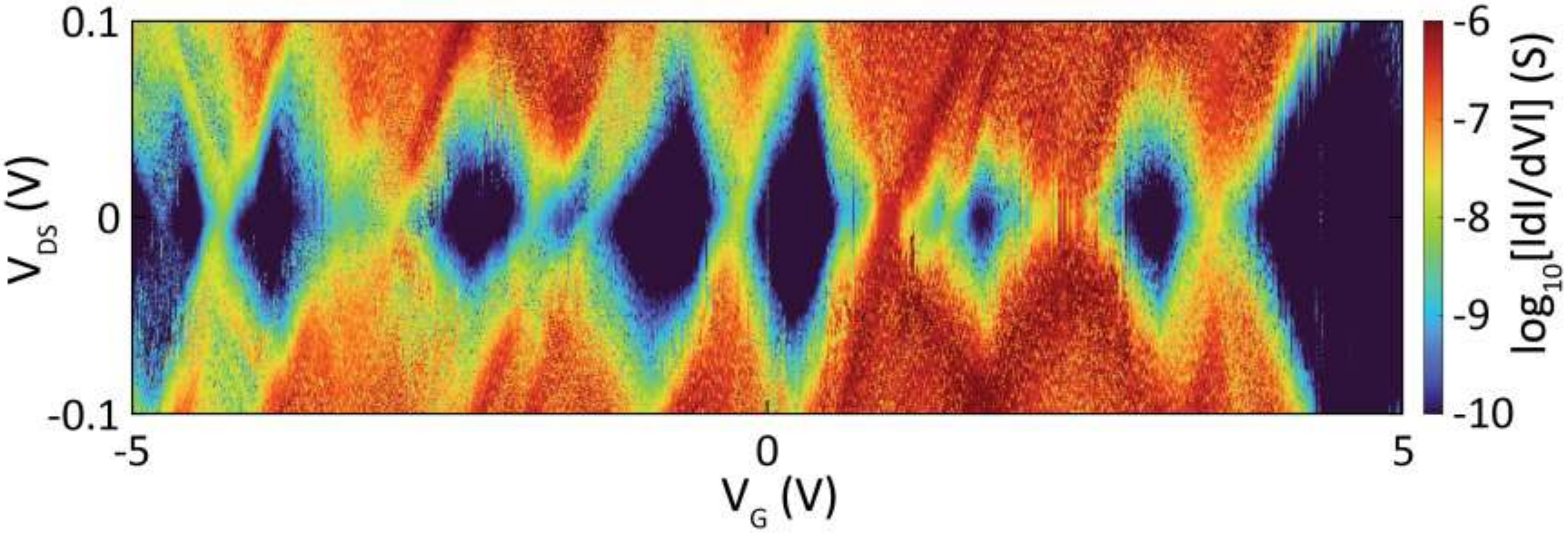
- Atomically smooth substrates
- Small lattice mismatch
- **Charge trap-free dielectric**
- Encapsulation, preventing material degradation
- Small footprint, reduced contact length
- Polymer-free contacts at the edge



Huang et al. ACS Nano, 2023

More on Contacts and Environment

Passivation and Edge Contacts

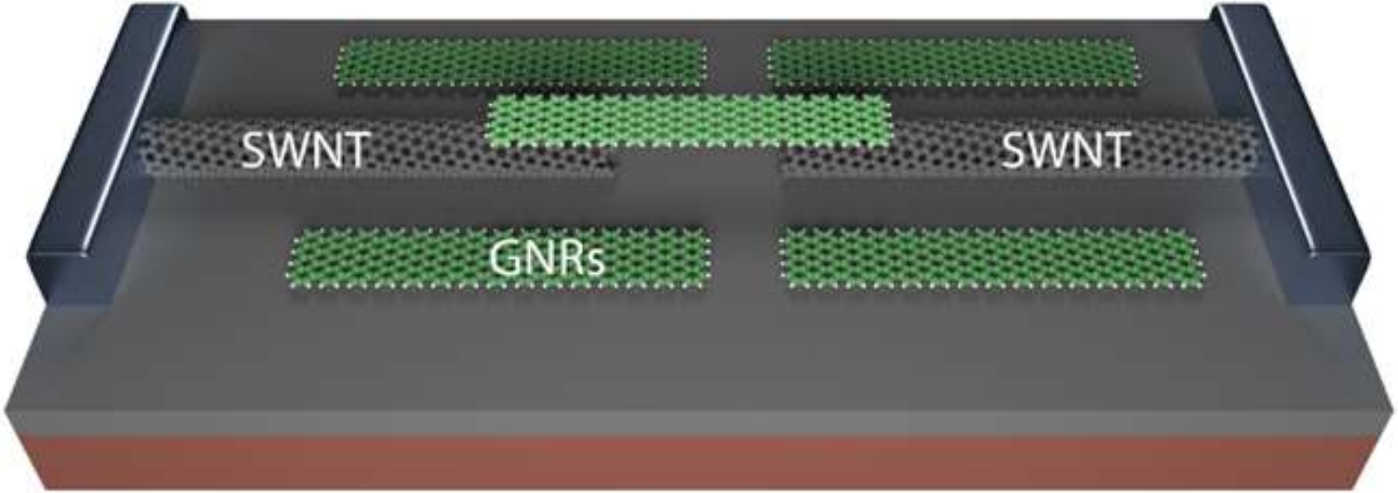


Huang et al. ACS Nano, 2023

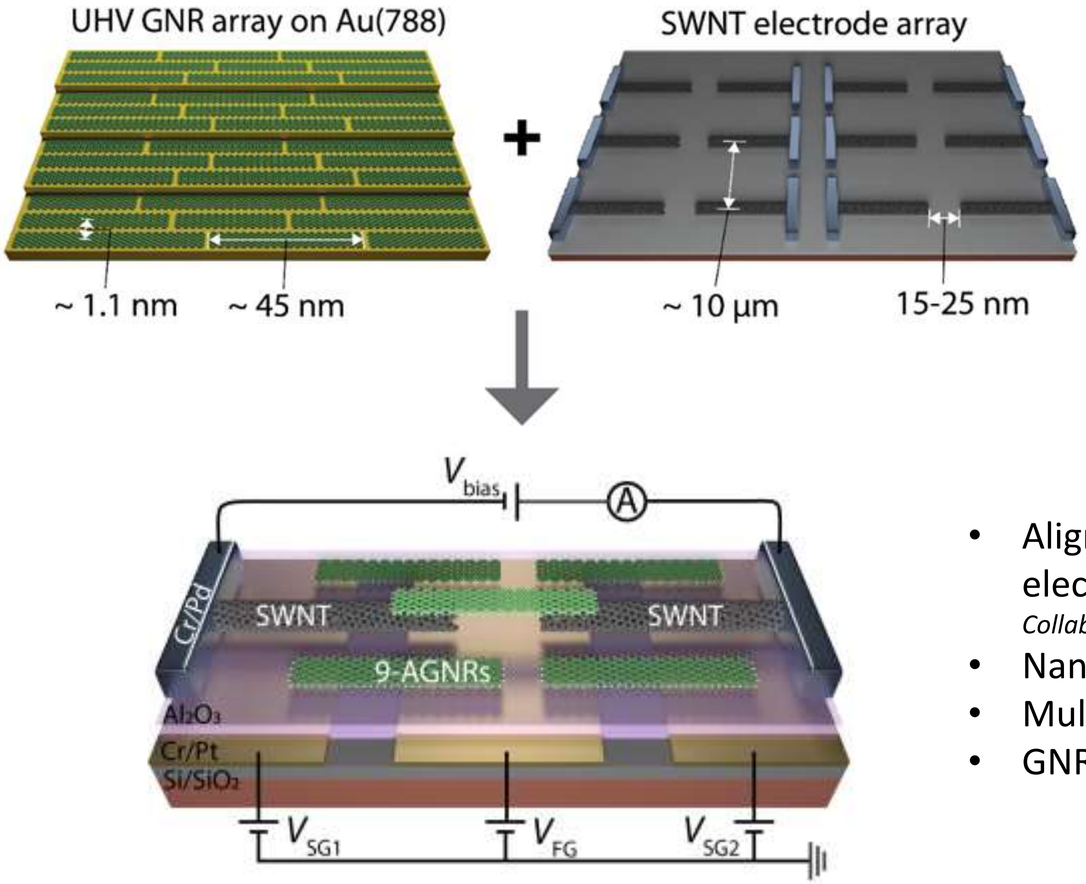
- Quantum dot behavior (9 K)

Ultimate (?) Contacts : Carbon Nanotubes

Controlled contacting of individual GNRs



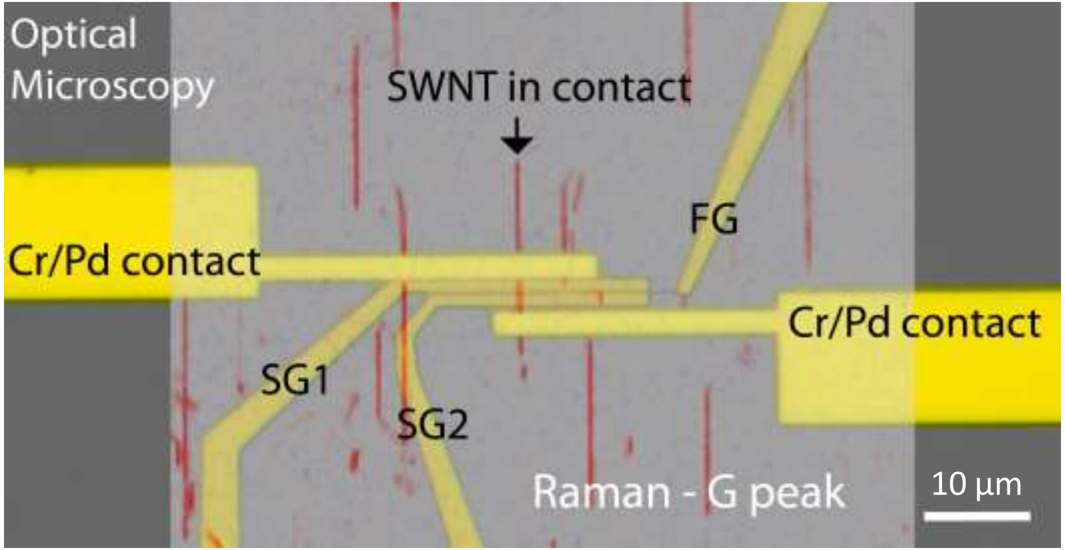
Ultimate (?) Contacts : Nanotubes

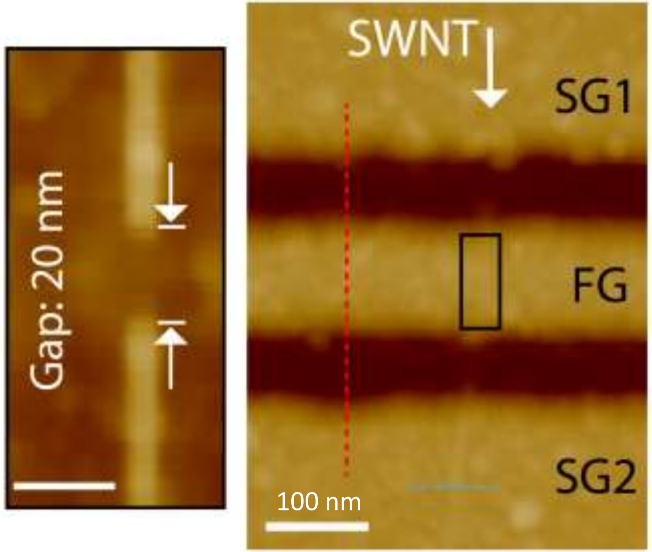


- Aligned **single-wall carbon nanotubes** as electrodes
  *Collaboration with **Prof. Jin Zhang** & Dr. Liu Qian*
- Nanogap formed using e-beam lithography
- Multiple gates
- GNRs last

Zhang et al., Nat. Electronics (2023)

GNR - Carbon Nanotubes Devices

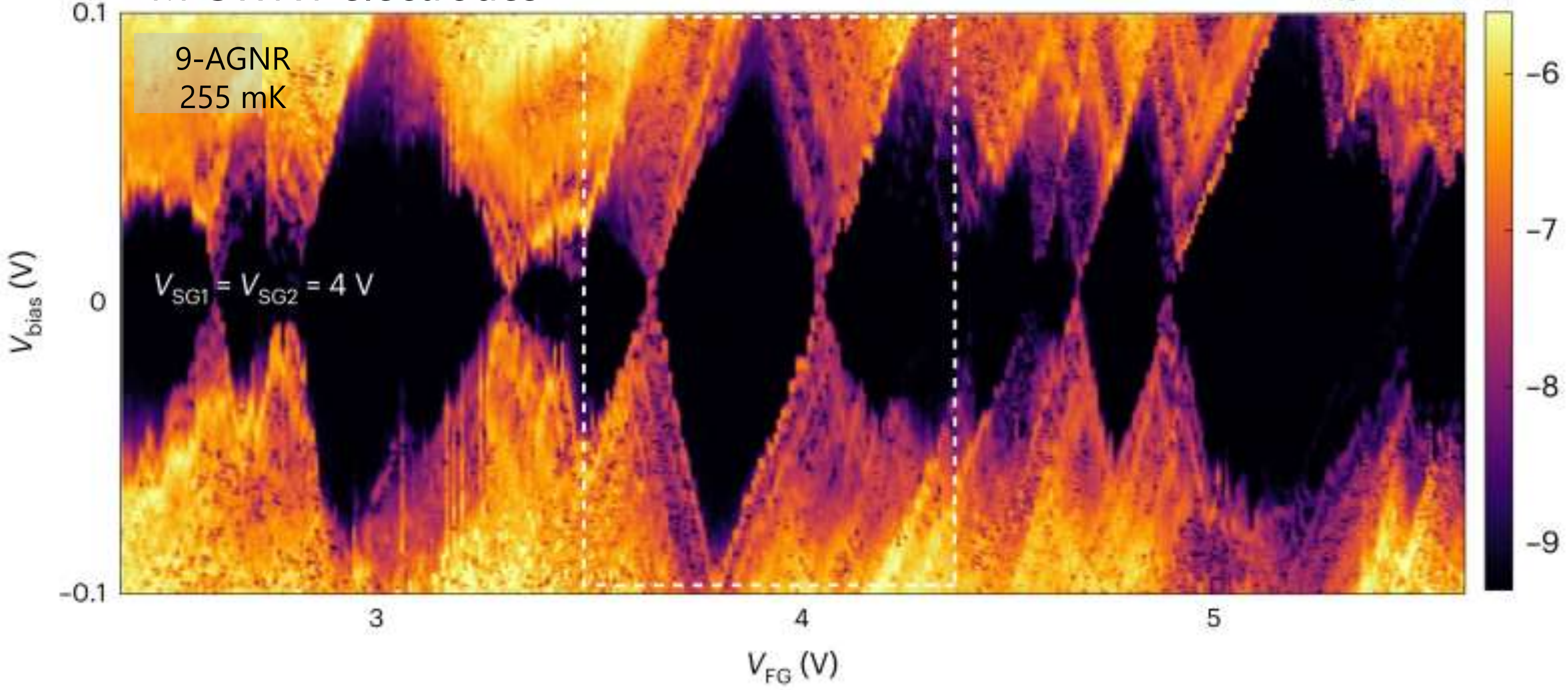




Zhang et al., Nat. Electronics (2023)

GNR - Carbon Nanotubes Devices

M-SWNT electrodes

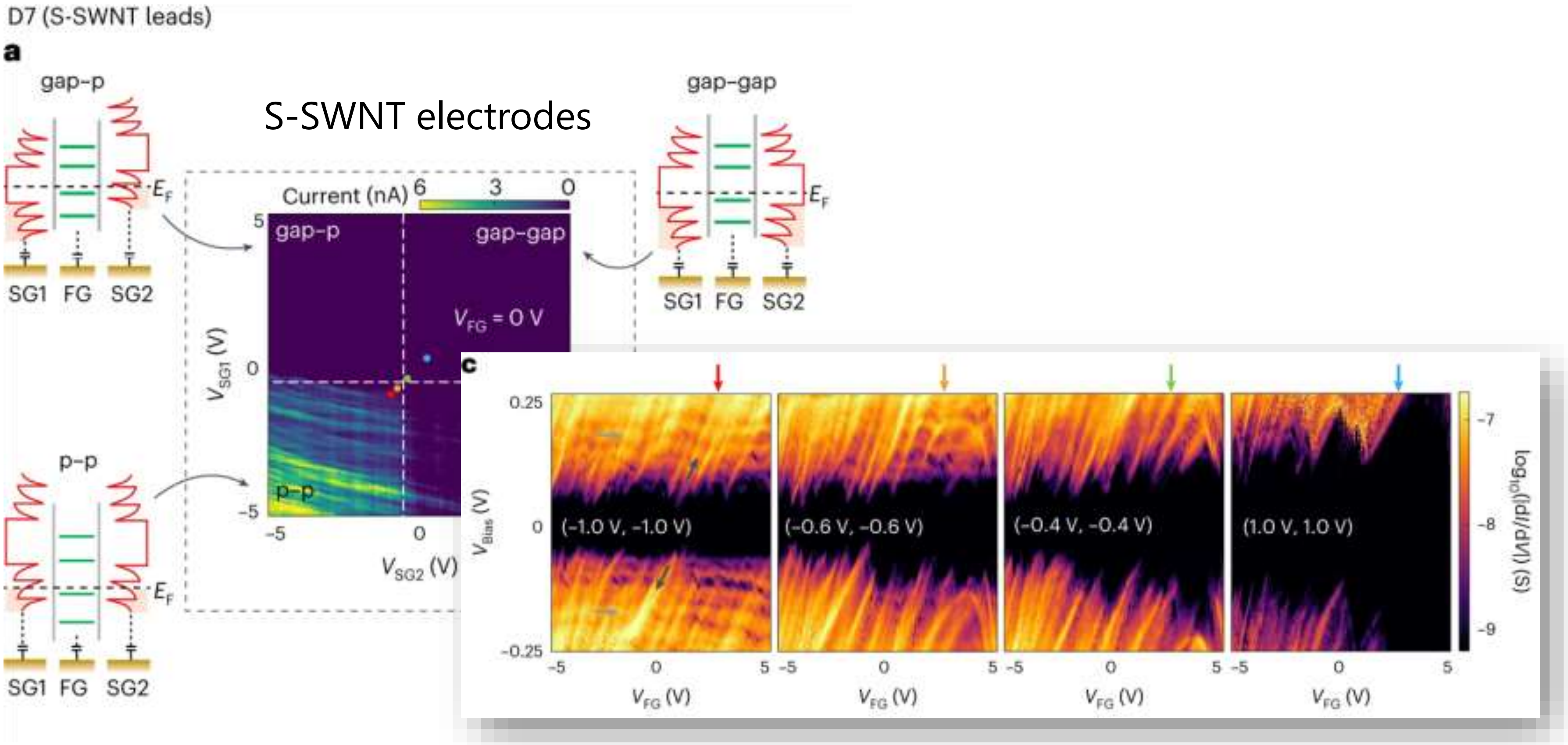


Well-defined Coulomb diamonds observed, including excitations in the SET regime

Zhang et al., Nat. Electronics (2023)

GNR - Carbon Nanotubes Devices

S-SWNT electrodes



Zhang et al., Nat. Electronics (2023)

Thermoelectric response in nanomaterials

Enhancing Thermoelectric Effects

Lyndon Hicks, Mildred Dresselhaus, 1993

PHYSICAL REVIEW B VOLUME 47, NUMBER 19 15 MAY 1993-I

Effect of quantum-well structures on the thermoelectric figure of merit

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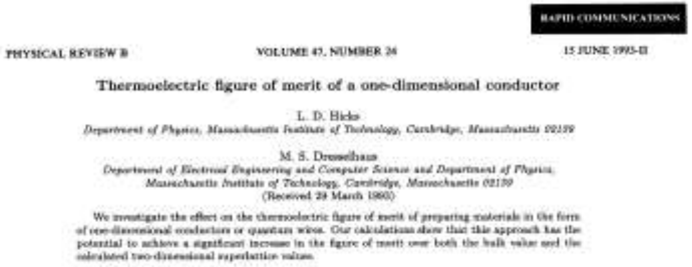
Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

M. S. Dresselhaus
Department of Electrical Engineering and Computer Science and Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 3 December 1992)

Currently the materials with the highest thermoelectric figure of merit Z are Bi_2Te_3 alloys. Therefore these compounds are the best thermoelectric refrigeration elements. However, since the 1960s only slow progress has been made in enhancing Z, either in Bi_2Te_3 alloys or in other thermoelectric materials. So far, the materials used in applications have all been in bulk form. In this paper, it is proposed that it may be possible to increase Z of certain materials by preparing them in quantum-well superlattice structures. Calculations have been done to investigate the potential for such an approach, and also to evaluate the effect of anisotropy on the figure of merit. The calculations show that layering has the potential to increase significantly the figure of merit of a highly anisotropic material such as Bi_2Te_3, provided that the superlattice multilayers are made in a particular orientation. This result opens the possibility of using quantum-well superlattice structures to enhance the performance of thermoelectric coolers.

Phonon glass/electric crystal



RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 47, NUMBER 24 15 JUNE 1993-II

Thermoelectric figure of merit of a one-dimensional conductor

L. D. Hicks
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M. S. Dresselhaus
Department of Electrical Engineering and Computer Science and Department of Physics, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 29 March 1993)

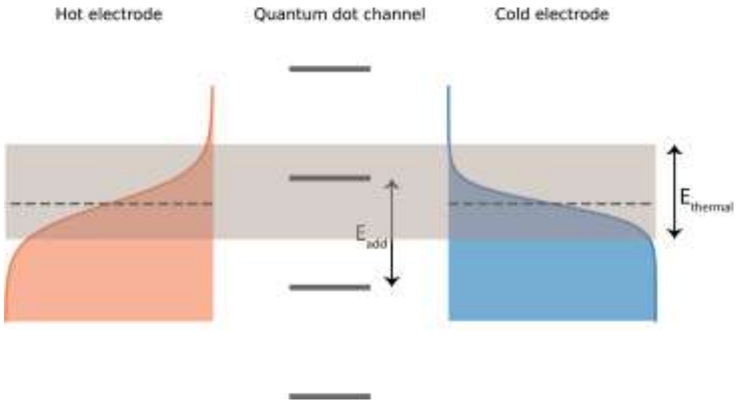
We investigate the effect on the thermoelectric figure of merit of preparing materials in the form of one-dimensional conductors or quantum wires. Our calculations show that this approach has the potential to achieve a significant increase in the figure of merit over both the bulk value and the calculated two-dimensional superlattice values.

- **Graphene not ideal**
  Gapless ⇨ small S (opp. contrib of e & h); excellent thermal conductor
- **Nanostructuring & Band gap engineering: GNRs & CNTs**

See for instance (GNRs)

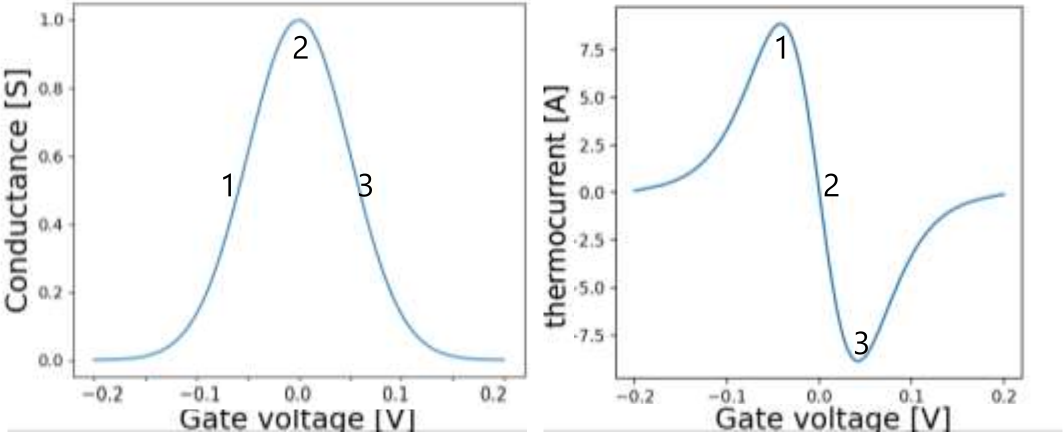
- Li et al., Nanostructured and Heterostructured 2D Materials for Thermoelectrics, Eng. Science 13, 24 (2021)
- Massetti et al., Unconventional Thermoelectric Materials for Energy Harvesting and Sensing Applications, Chem. Rev. 121, 12465 (2021)
- Dollfus et al., Thermoelectric effects in graphene nanostructures, J. Phys.: Cond. Matt. 27, 133204 (2015)

Thermoelectrical behaviour expected



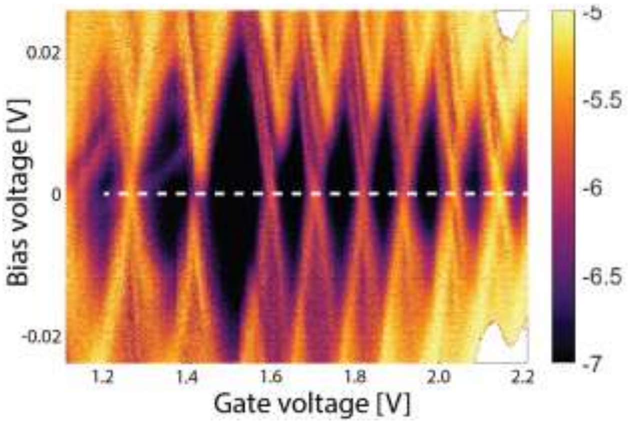
- Window for thermoelectric transport ($E_{thermal}$) scales with T
- High efficiency:
  - only single level within the window
  - E_{add} > $E_{thermal}$
- Demonstrated so far: E_{add} < 5meV

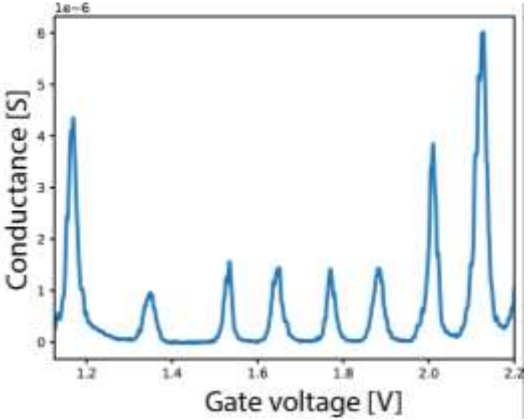
- Sign change for thermoelectric current
- Theoretical gate characteristic for single level:



Frederik Van Veen et al.

Carbon Nanotube Qdot (4K)

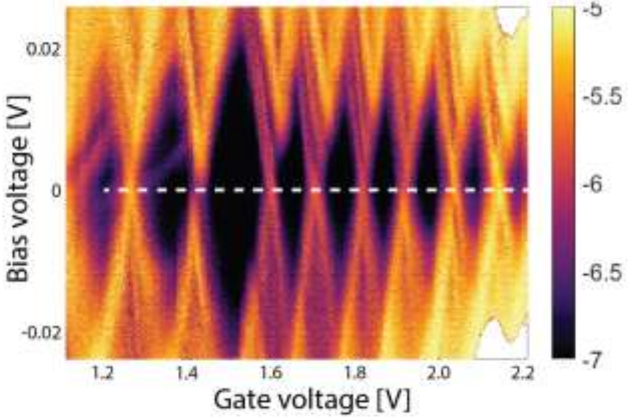


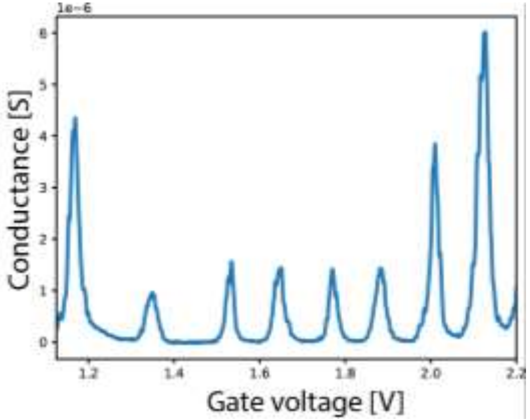


- No interface barriers (closing diamonds)
- Zero-bias gatesweep shows clean peaks
- Addition energies of ~20 meV

Frederik Van Veen et al.

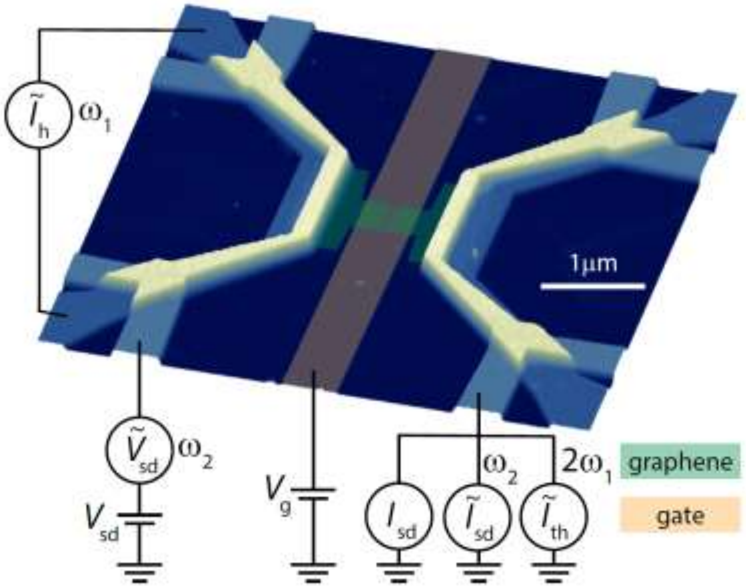
Carbon Nanotube Qdot (4K)





Measurement principle

Equivalent Seebeck coefficient: $\frac{I_{th}}{G} \cdot \frac{1}{\Delta T}$ $G = \frac{dI}{dV}$

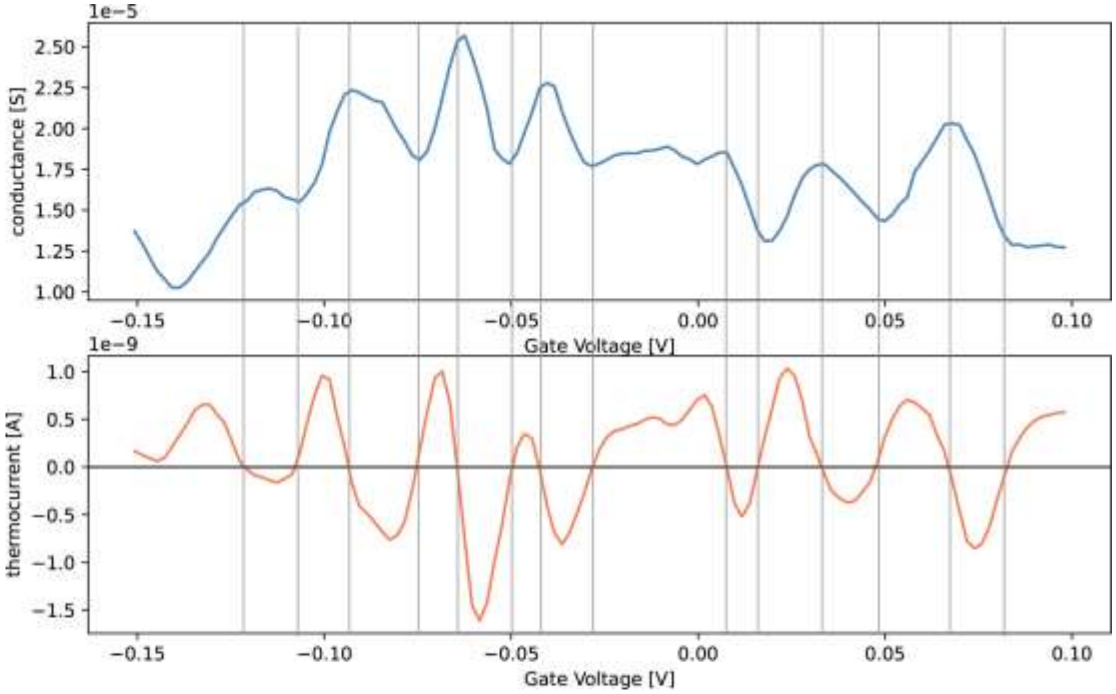


GΩ impedance: Double- modulation technique

Similar approach as Gehring *et al.*, APL (2019) & Nat. Nanotech (2021)

Frederik Van Veen et al.

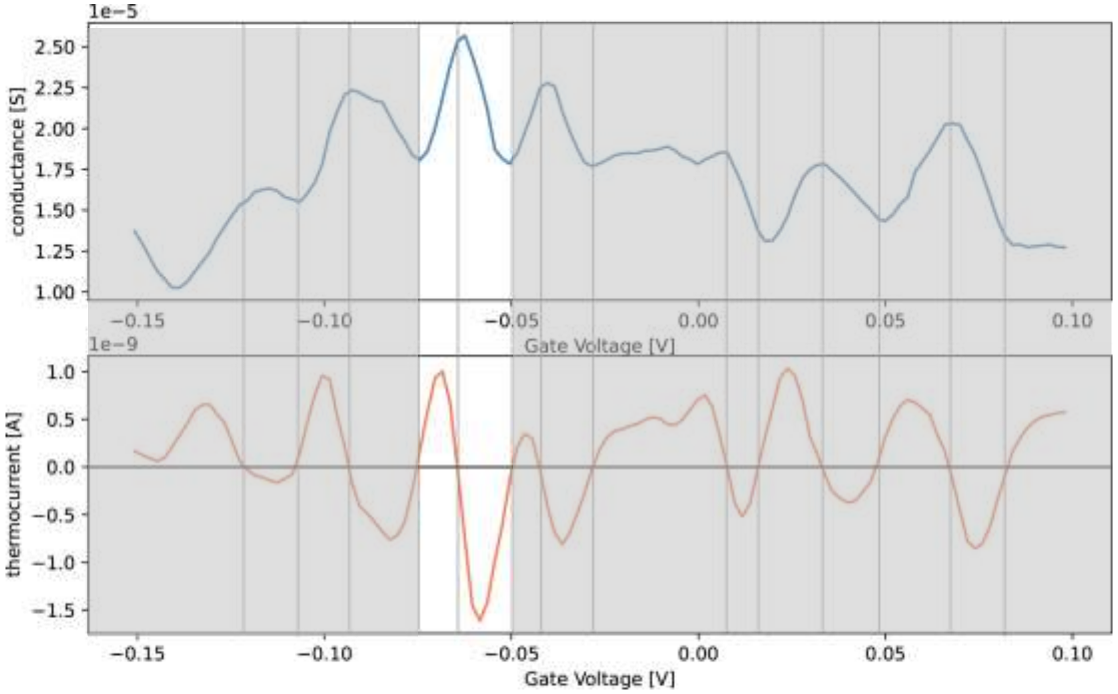
Thermoelectrical measurement on CNT Qdot



- Every conductance peak correspond to a single level
- For each peak we observe the characteristic sign-changing curve
- Generated current can be controlled electrostatically

Frederik Van Veen et al.

Thermoelectrical measurement on CNT Qdot



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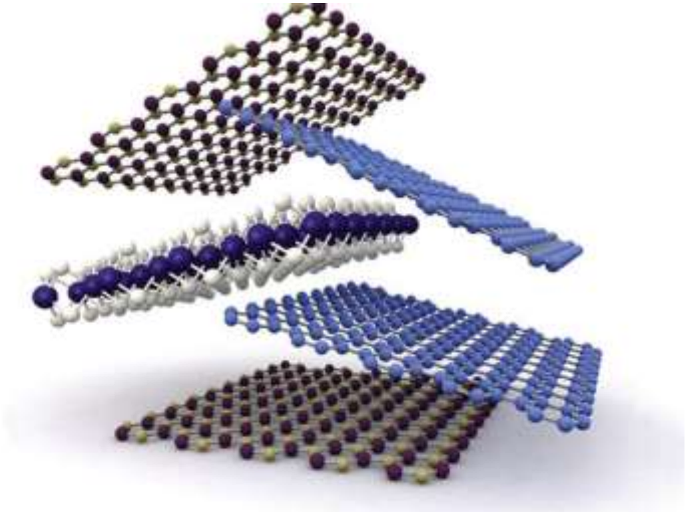
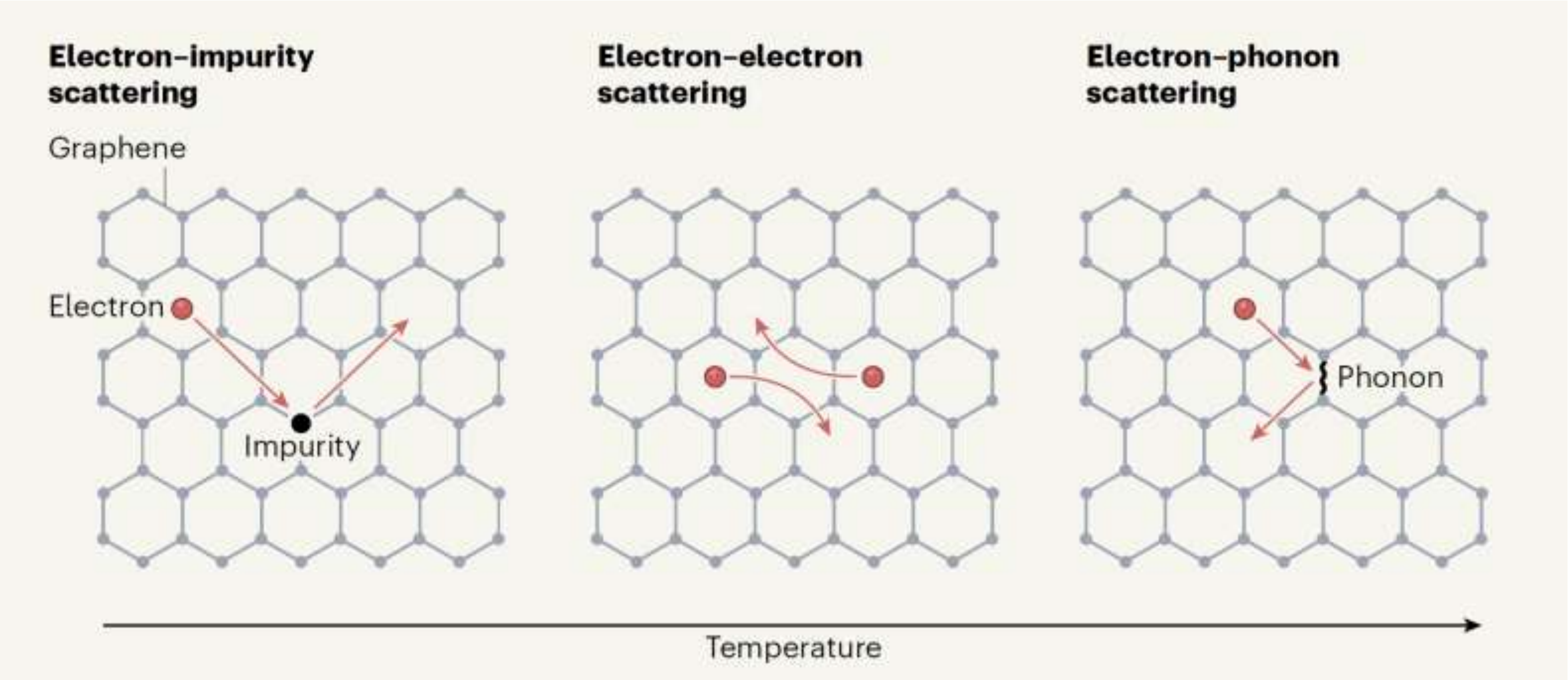
Frederik Van Veen et al.



Novoselov *et al.* Science (2016)

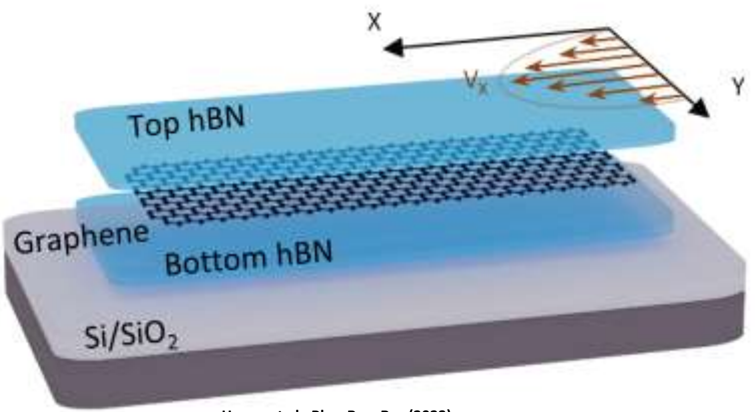
Exotic Transport Regime: Electron hydrodynamics



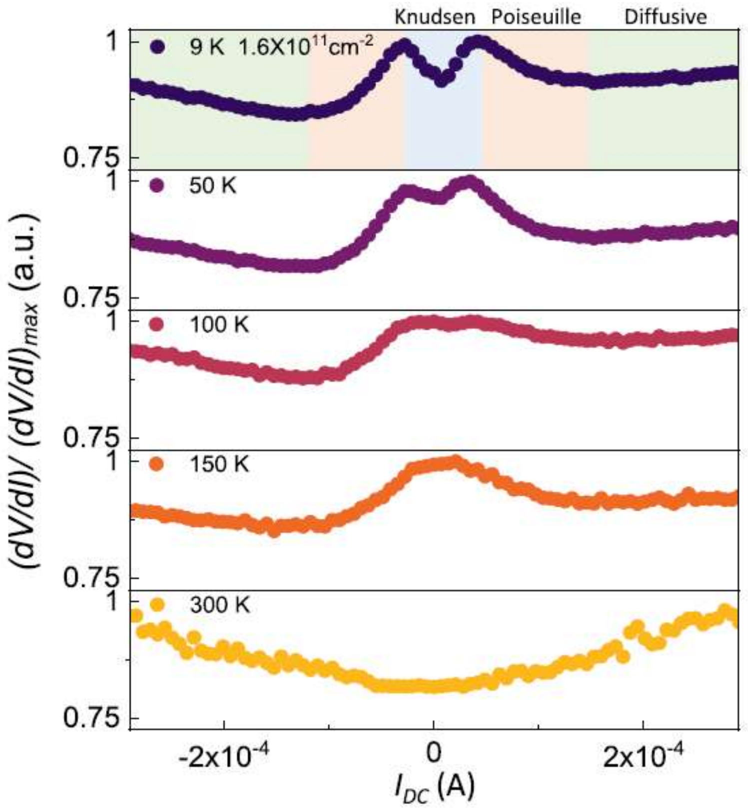
Ensslin, Nature n&v (2019)

Exotic Transport Regime: Electron hydrodynamics

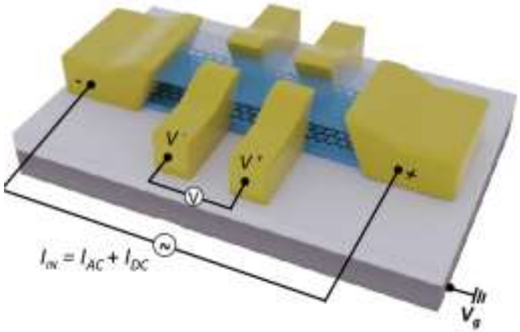
Encapsulated Graphene

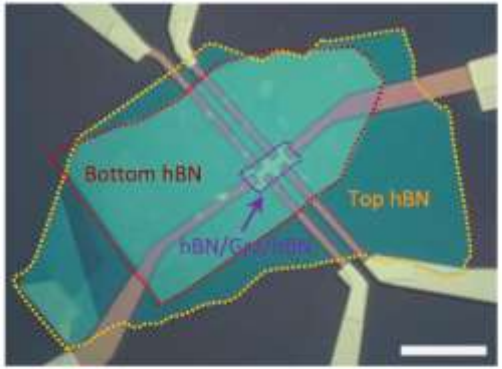


Huang et al., Phys Rev. Res (2023)



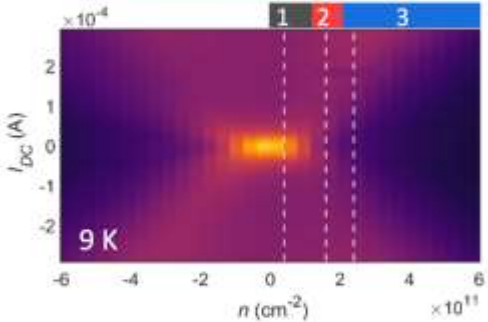
Exotic Transport Regime: Electron hydrodynamics

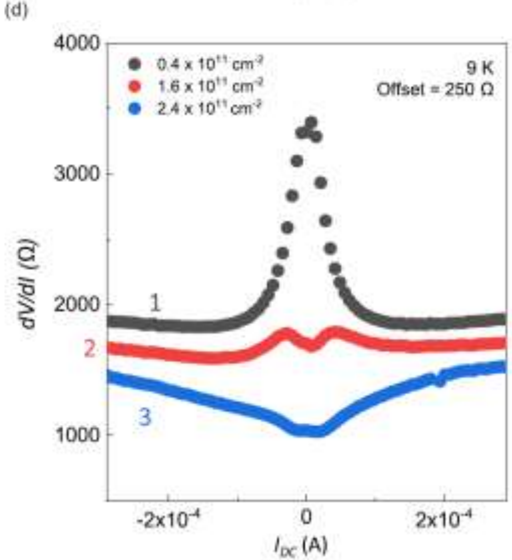




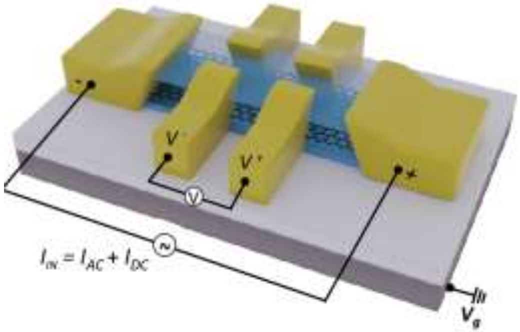
Huang et al., Phys Rev. Res (2023)

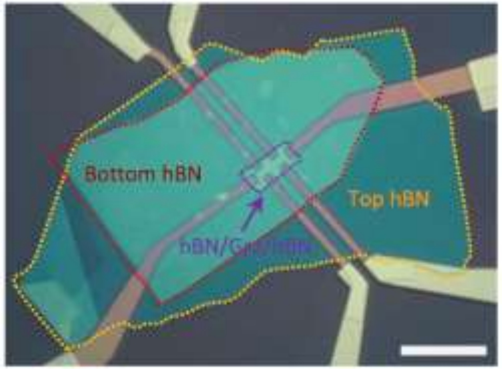
R dependence on charge carrier density at 9K





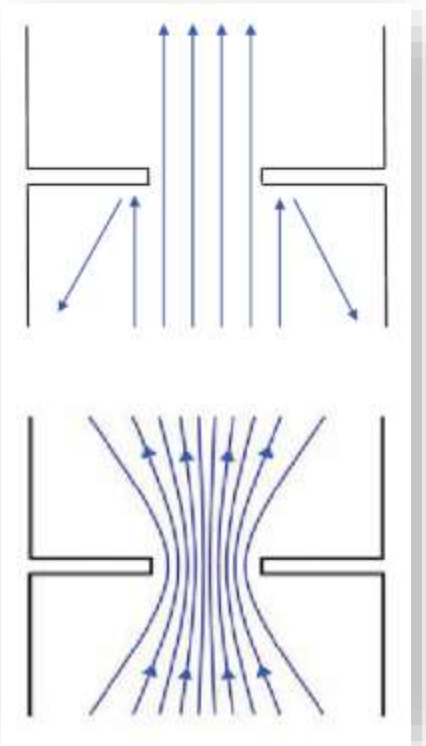
Exotic Transport Regime: Electron hydrodynamics





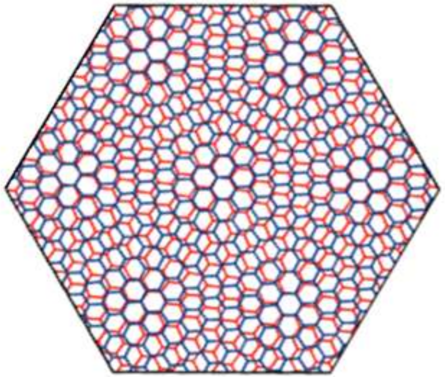
Huang et al., Phys Rev. Res (2023)

⇨ Engineer electron flow to improve energy efficiency / enable conductance beyond ballistic and Landauer-Sharvin limits



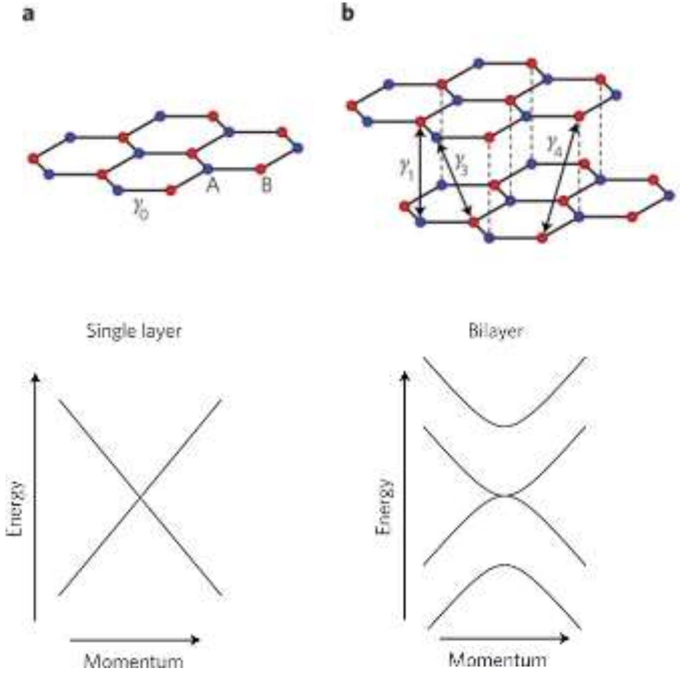
Moiré systems: Band engineering in 2D materials

Twisted n-layer graphene



Zhang, Perrin et al., under review

Bilayer graphene: two layers shifted with respect to each other, the B atoms of one are situated directly above the A atoms of the other

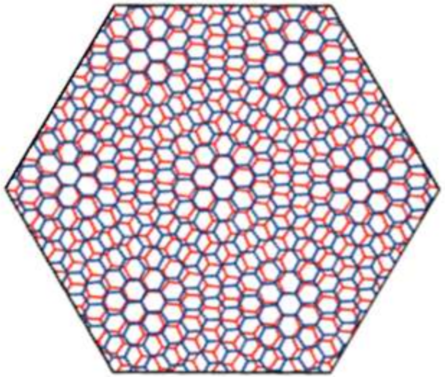


M. Freitag, Nat. Phys. 2011

- massive chiral Fermions (no QED equivalent)
- higher energy subbands do not contribute to transport (unless high doping)

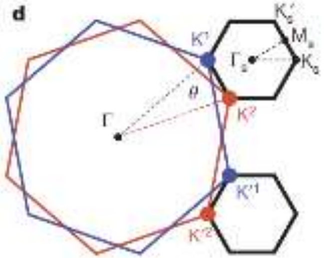
Moiré systems: Band engineering in 2D materials

Twisted
n-layer graphene

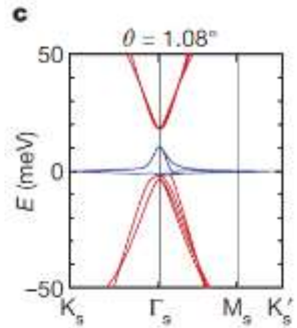


Zhang, Perrin et al., under review

Twisted bilayer graphene



Moiré bands in twisted double-layer graphene
***Bistritzer** & McDonald, PNAS (2011)*



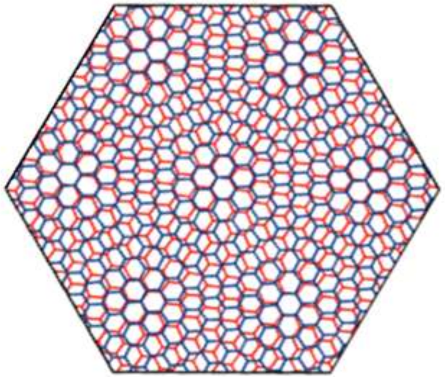
Band energy E of magic-angle (θ = 1.08°).
TBG calculated using an
ab initio tight-binding method

Superconductivity for angles leading to "flat bands"

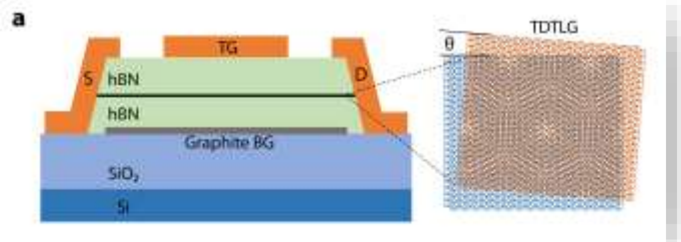
E. Mele, Nature n&v (2018)
P. Jarillo-Herrero et al., Nature (2018)

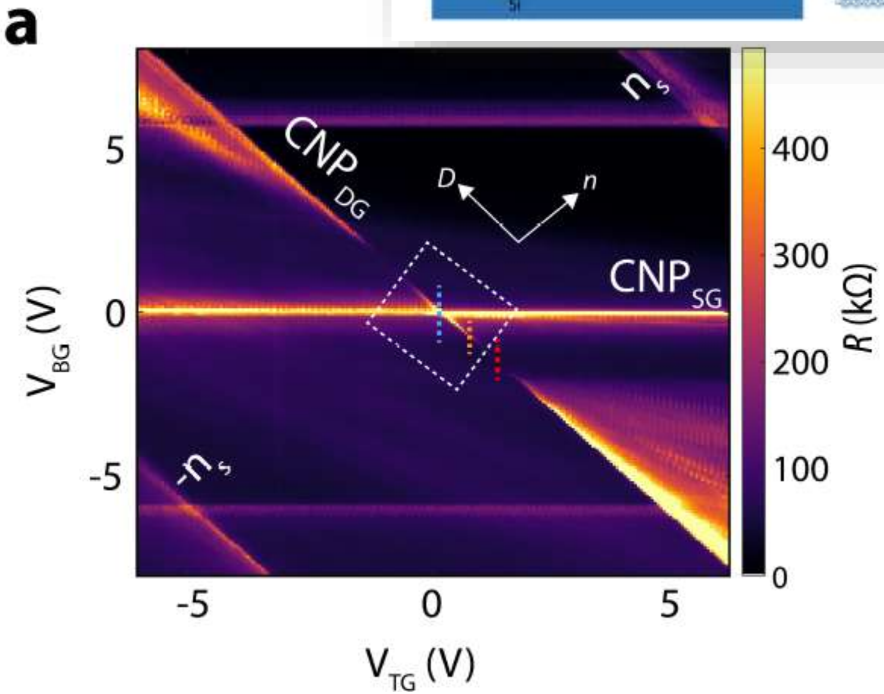
Moiré systems: Band engineering in 2D materials

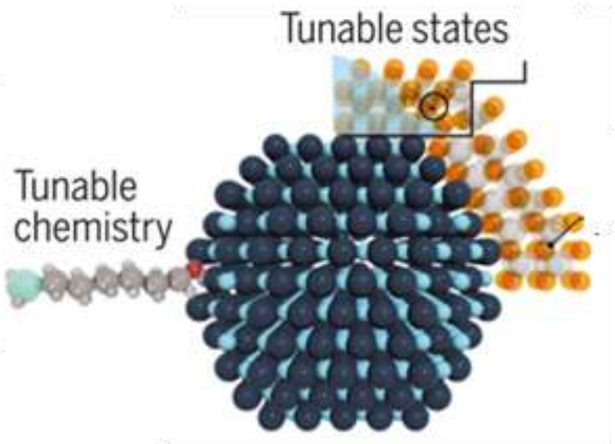
Twisted n-layer graphene



Zhang, Perrin et al., under review



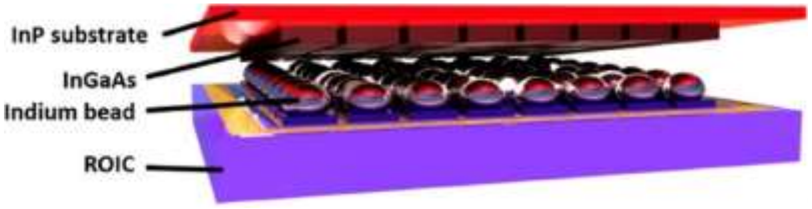




de Arquer *et al.* Science (2021)

Colloidal Quantum Dots (cQDs) for IR imaging

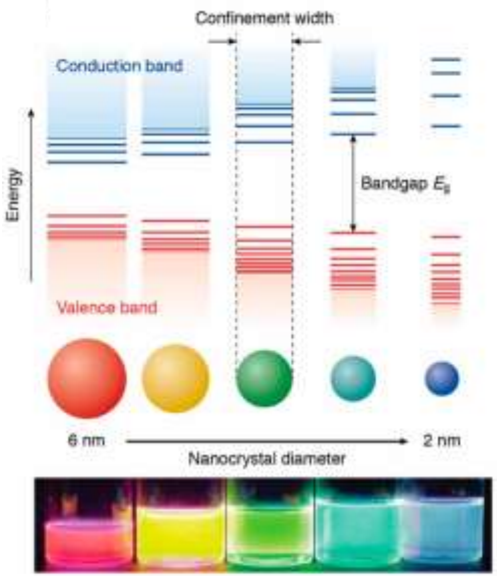
State-of-the-art



Solution-processable photoactive material

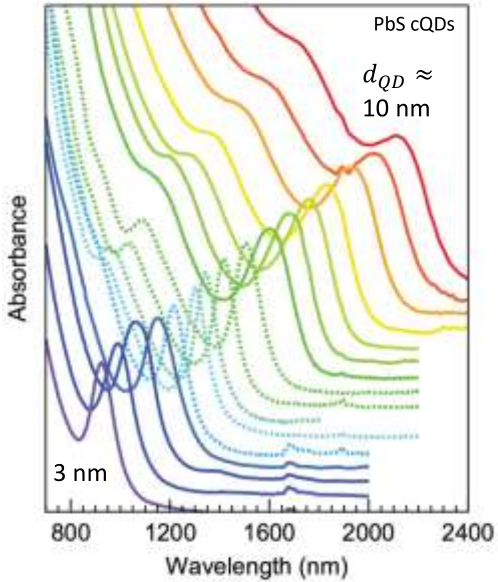
Gréboval et al. *Chem. Rev.* 2021. https://doi.org/10.1021/acs.chemrev.0c01120.

cQDs: Size tunable optical properties



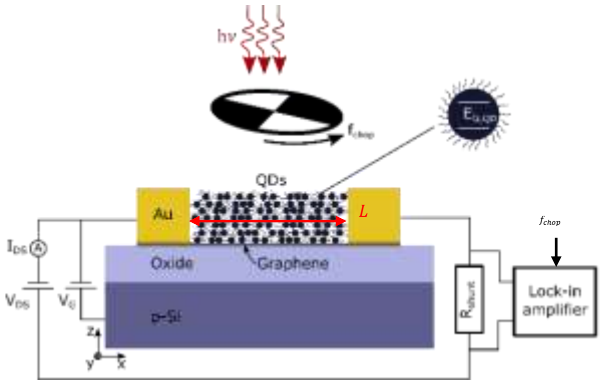
CdSe cQDs

Berends et al. *J. Phys. Chem. Lett.* **2017**.
https://doi.org/10.1021/acs.jpclett.7b01640.

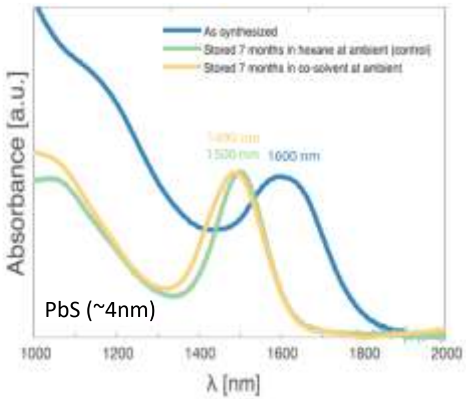


Moreels et al. *ACS Nano* **2011**, *5* (3), 2004–2012.
https://doi.org/10.1021/nn103050w.

Photodetectors from printed cQDs



Original idea: Konstantatos, …& Koppens, Nat. Nanotechnol. (2012)



Kara et al., Adv. Mat. Tech. (2023)

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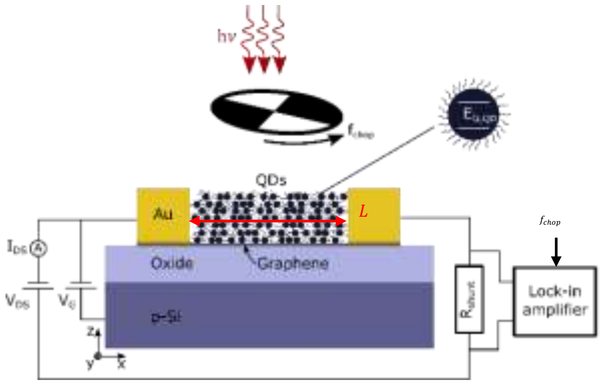
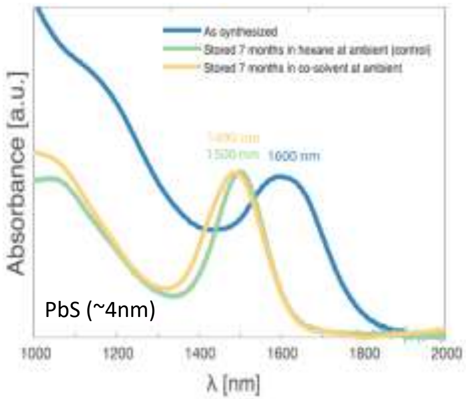
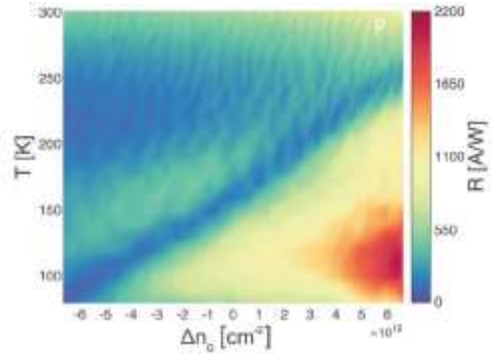


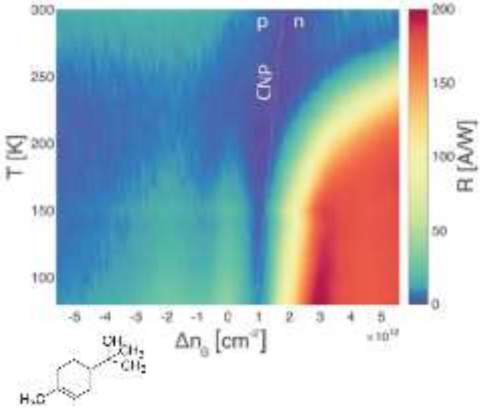
Original idea: Konstantatos, …& Koppens, Nat. Nanotechnol. (2012)



Qdots solvent: hexane (C_6H_{14})



Qdots solvent: a-Terpineol



Kara et al., Adv. Mat. Tech. (2023)

Responsivity maps for 2 different Qdots solvents
vs charge carrier density and Temperature

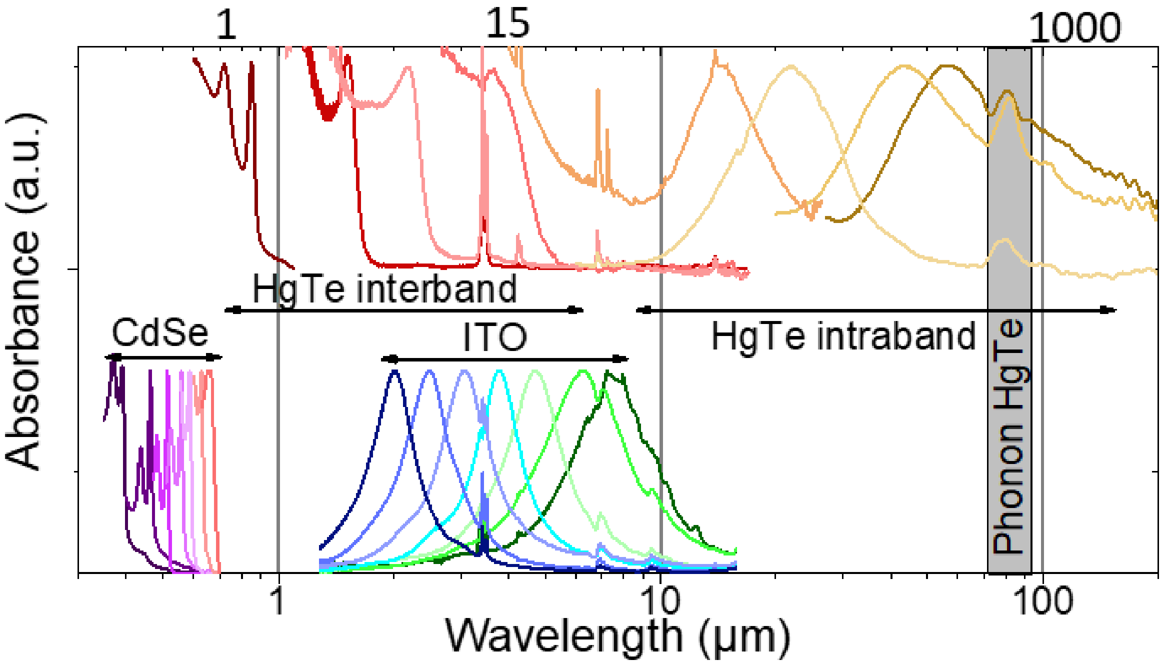
Responsivity

$$R = \frac{I_{ph}}{P_{in}}$$

⇨ Importance of processing

Printing, Ink viscosity, pinning of dots on substrate, packing/order of qdot film; ligand & ligand exchange

Extensive tunability: HgTe



- Spectral tunability over two orders of magnitude
- Combine interband, interband and plasmonic absorption
- *Single photon counting ?*

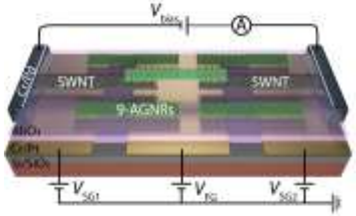
NB: **perovskite** materials
X-ray absorption (10-30keV)
See e.g. Kovalenko et al. Nat. Photonics (2023)

C. Greboval et al, Chem Rev 121, 3627 (2021).

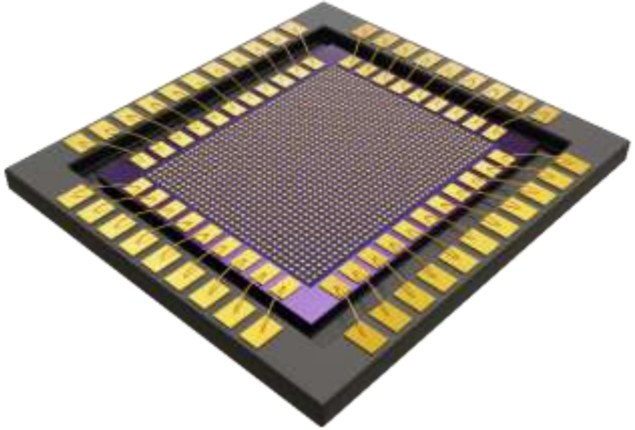
Adapted from E. Lhuillier

Upscaling … ?

One device



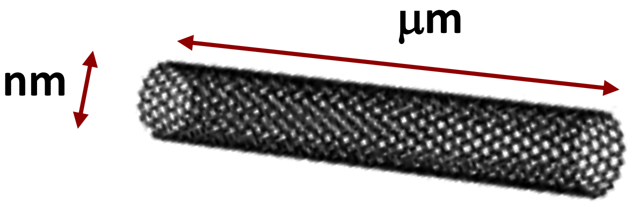
M x N devices

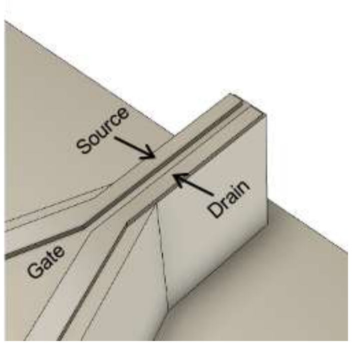


Automatization of the Nanomaterials Integration

Strategic Focus Area
Advanced Manufacturing

with nanostructures - 1 million x smaller





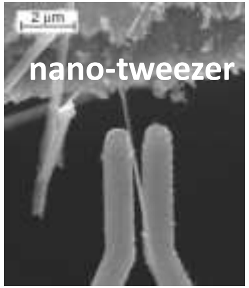
Eberle et al., Microelec. Eng. *(10.1016/j.mee.2018.02.027)*

Source: ABB, https://new.abb.com/products/robotics/industrial-robots/irb-360

State-of-the-art - Nanomaterials integration

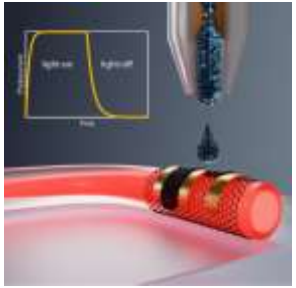
Pick and place

Ye et al., IEEE Trans. Automation Sci. & Eng. (2013)



P. Bögglid et al., Nanotech. 17 (2006)

Alternative techniques, e.g.: Printing



Kara *et al.,* Adv. Mater. Technol. (2023)

Electrohydrodynamic Printing of Synthetic Qdots Inks

e.g. HgTe, PbS

Synthesis: M. Kovalenko *et al.*

Devices: I. Shorubalko et al.

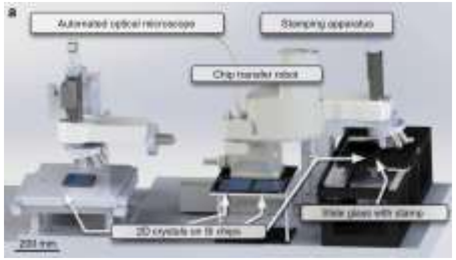
Shorubalko *et al.,* Nat. Photonics (2022)

Grotevent *et al.,* US Patent 11,067,442, 2021

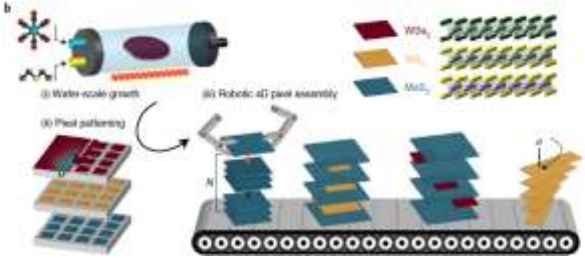
www.scrona.com

Robotic assembly of Nanomaterials

R. Frisenda, A. Castellanos-Gomez, News &Views Nature Nano, 13 (2018) 441



S. Masubuchi et al., Nature Comm. (2018) 9:1413

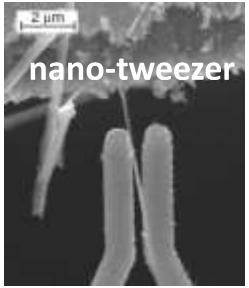


Mannix et al., Nature Nanotech. (2022)

State-of-the-art - Nanomaterials integration

Pick and place

Ye et al., IEEE Trans. Automation Sci. & Eng. (2013)



P. Bögglid et al., Nanotech. 17 (2006)

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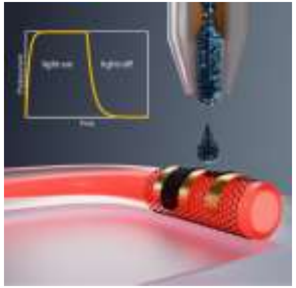

Kara *et al.,* Adv. Mater. Technol. (2023)

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e.g. HgTe, PbS
Synthesis: M. Kovalenko *et al.*
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Shorubalko *et al.,* Nat. Photonics (2022)
Grotevent *et al.,* US Patent 11,067,442, 2021
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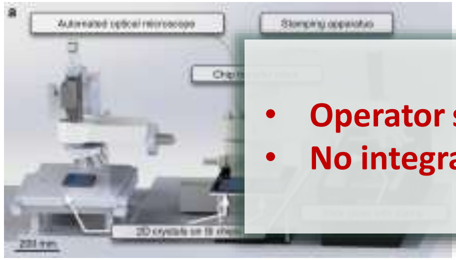
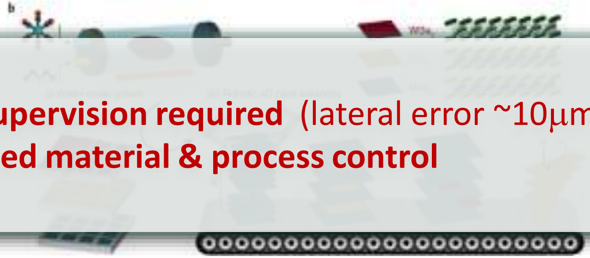


S. Masubuchi et al., Nature Comm. (2018) 9:1413

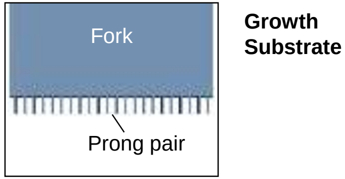


Mannix et al., Nature Nanotech. (2022)

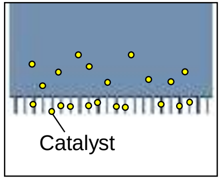
- **Operator supervision required** (lateral error ~10µm)
- **No integrated material & process control**

Manufacturing process overview

Substrate Fabrication

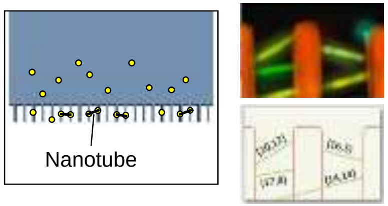


Catalyst Deposition

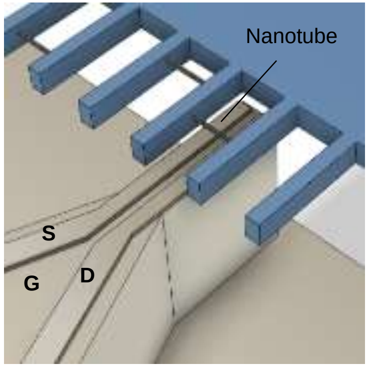


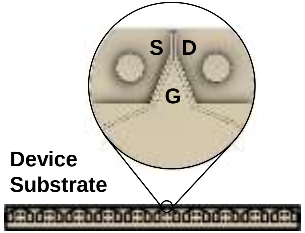
Nanotube Growth

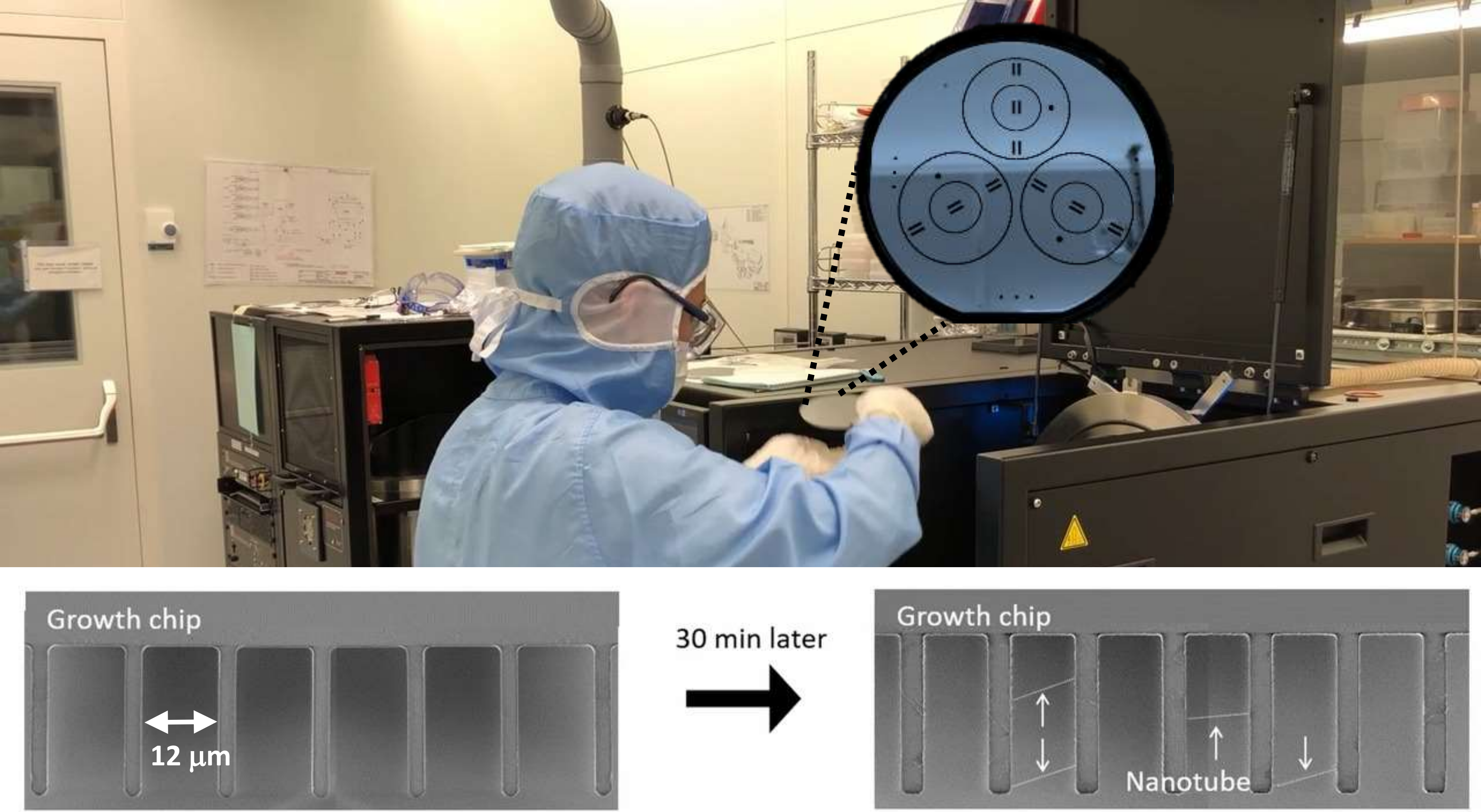
High-speed Raman Imaging and Machine Learning Classification



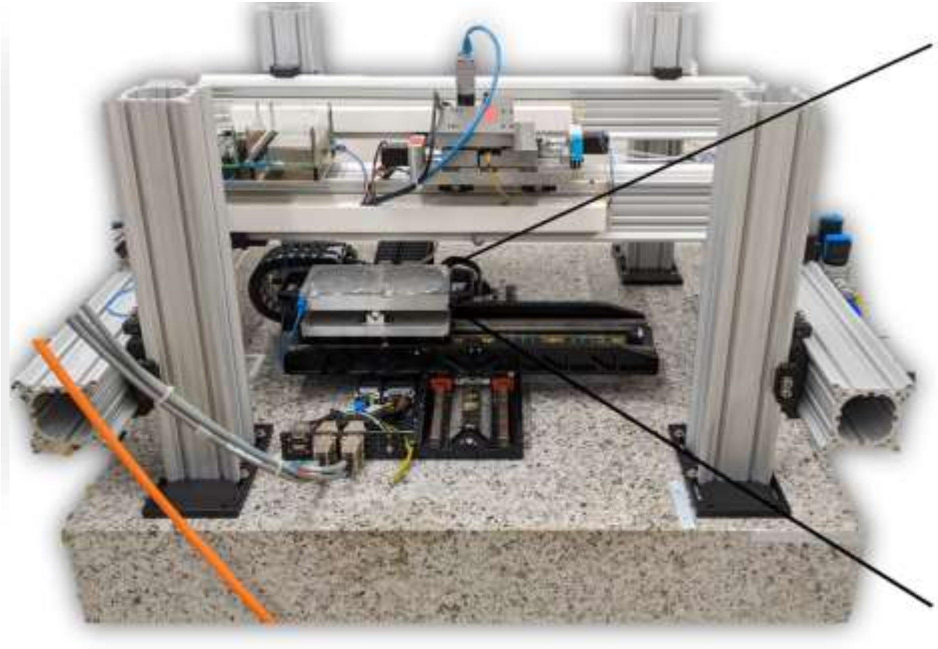
Automated CNT Transfer






Growth chip
12 μm
30 min later
Growth chip
Nanotube

Automatized Materials Integration
Carbon Nanotubes

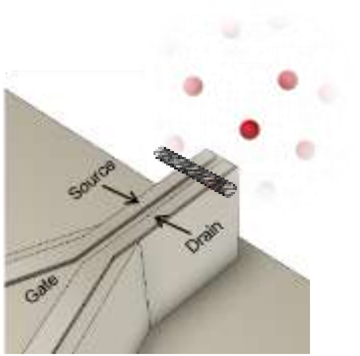


https://www.sfa-am.ch/nano-assembly.html

Potential Applications

Sensing Technology

Ultra-low power & portable sensors



Sensing
Gas molecules

NO_2 detection demonstrated (sub-ppm level);
Benchmarking to manually assembled devices

Satterthwaite *et al.,* Sens. Actuator B (2019)

NB: recovery is accelerated in our case using an external microheater

S. Jung *et al.* In preparation

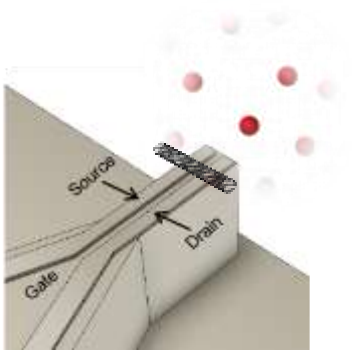
S. Jung et al., Sensors and Actuators B: Chemical, 331, 129406, (2020).

Potential Applications

Strategic Focus Area
Advanced Manufacturing

Sensing Technology

Ultra-low power & portable sensors



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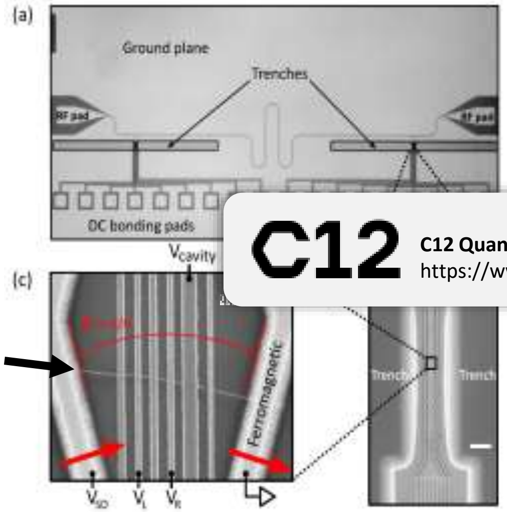
Quantum Technology

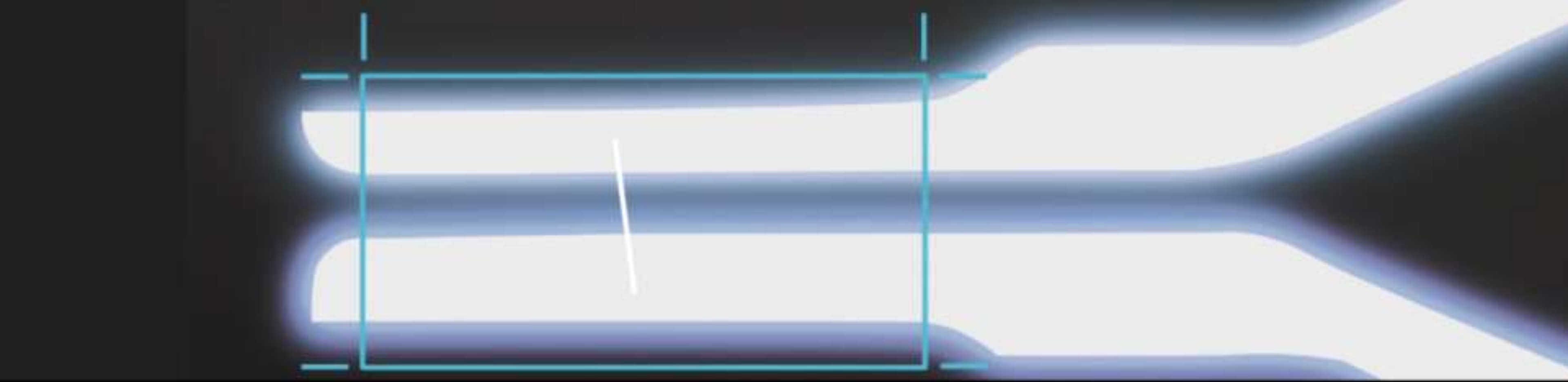
Qubits for circuit quantum electrodynamics

Carbon nanotube



C12
C12 Quantum Electronics
https://www.c12qe.com

Highly coherent spin states in carbon nanotubes coupled to cavity photons; Cubaynes *et al.*, npj Quantum Information 5:47 (2019)



chiral

https://www.chiralnano.com

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next-generation chips for sensors, quantum computers and more

Empa
Materials Science and Technology

Thank you

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www.empa.ch/tnilab

Fabrication Facilities

BRNC Binnig and Rohrer Nanotechnology Center

FIRST Center for Micro- and Nanoscience

Funding Agencies

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SNI

Strategic Focus Area Advanced Manufacturing

EU FP7 & H2020

MSCA