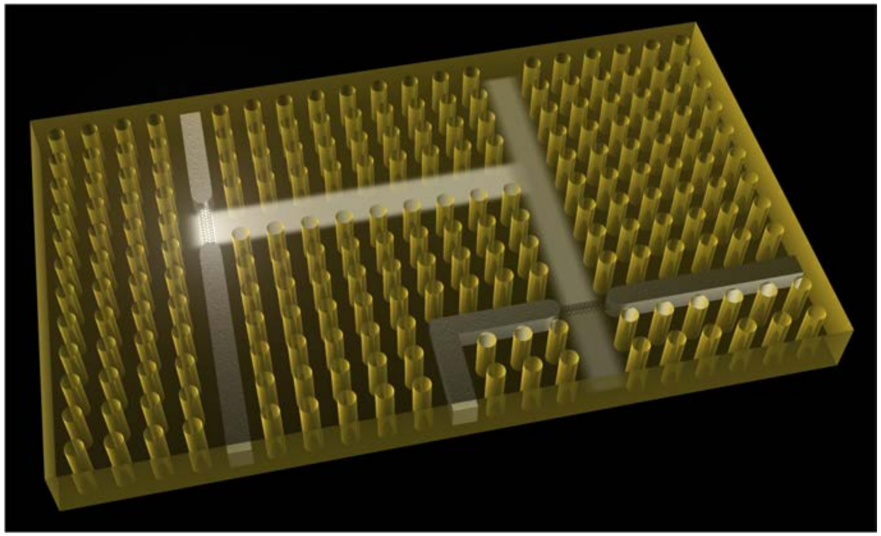
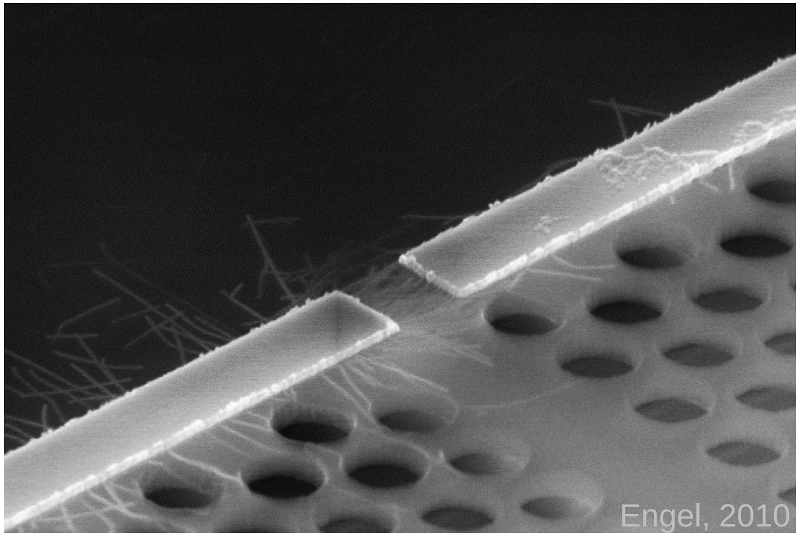
electroluminscence from carbon nanotubes - towards optoelectronics with on-chip light sources

Ralph Krupke

Institut für Nanotechnologie, Karlsruher Institut für Technologie (KIT), Germany
Institut für Materialwissenschaften, Technische Universität Darmstadt (TUD), Germany





Engel, 2010

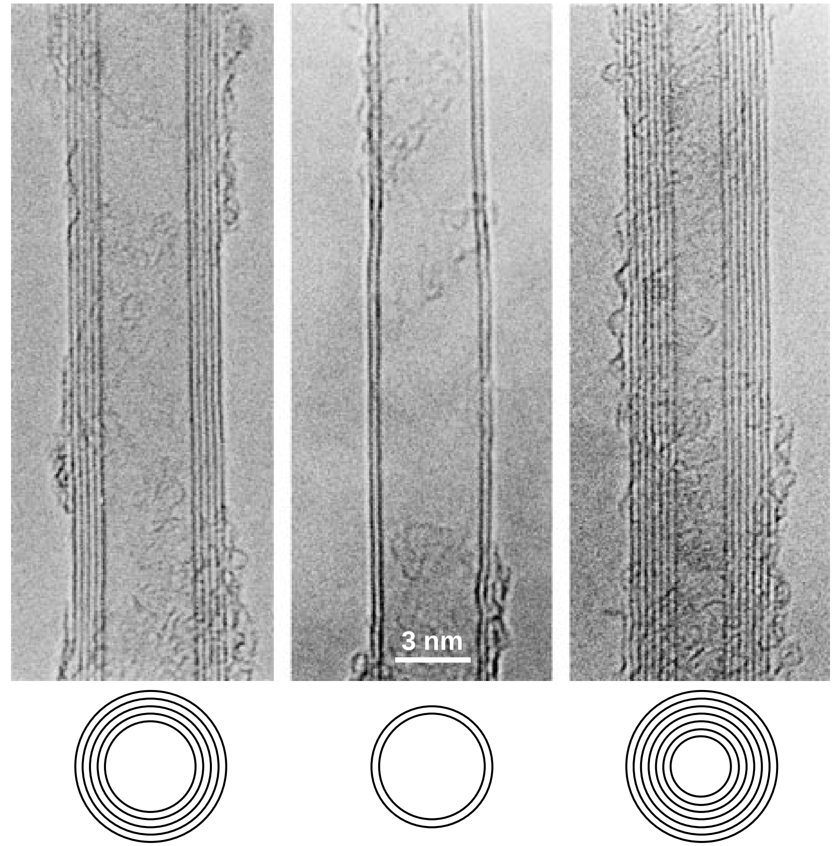
LETTERS TO NATURE

Helical microtubules of graphitic carbon

Sumio Iijima

NEC Corporation, Fundamental Research Laboratories,
34 Miyukigaoka, Tsukuba, Ibaraki 305, Japan

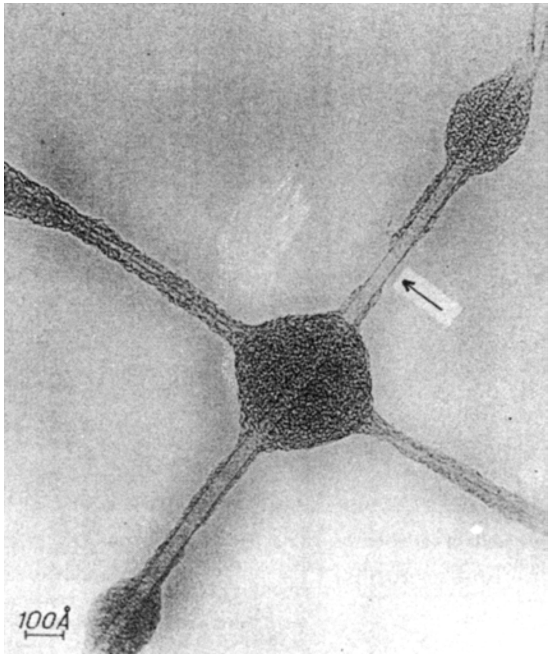
THE synthesis of molecular carbon structures in the form of C_{60} and other fullerenes[1] has stimulated intense interest in the structures accessible to graphitic carbon sheets. Here I report the preparation of a new type of finite carbon structure consisting of needle-like tubes. Produced using an arc-discharge evaporation method similar to that used for fullerene synthesis, the needles grow at the negative end of the electrode used for the arc discharge. Electron microscopy reveals that each needle comprises coaxial tubes of graphitic sheets, ranging in number from 2 up to about 50. On each tube the carbon-atom hexagons are arranged in a helical fashion about the needle axis. The helical pitch varies from needle to needle and from tube to tube within a single needle. It appears that this helical structure may aid the growth process. The formation of these needles, ranging from a few to a few tens of nanometres in diameter, suggests that engineering of carbon structures should be possible on scales considerably greater than those relevant to the fullerenes.



NATURE · VOL 354 · 7 NOVEMBER 1991

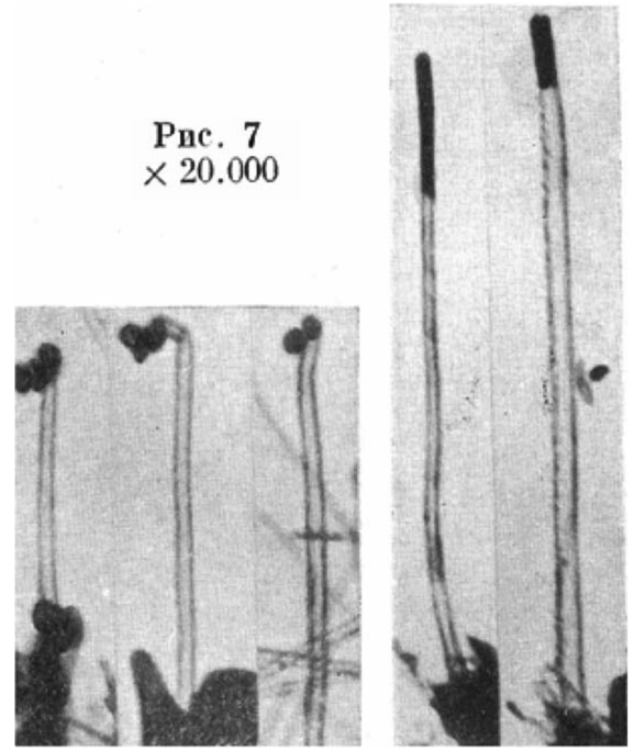
Historical perspective

5nm wide tubular struture (DWNT)



Oberlin, Endo, Koyama, Carbon 1976

50nm wide tubular structure (MWNT)



Radushkevich, Lukyanovich, Zurn Fisic Chim 1952

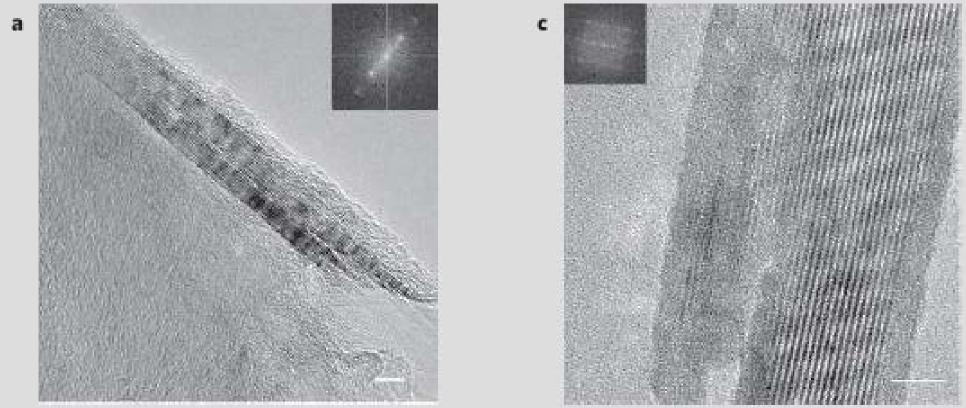
Monthioux, Kuznetsov, Carbon 44, 1621 (2006):
Who should be given the credit for the discovery of carbon nanotubes?

Historical perspective

Carbon nanotubes in an ancient Damascus sabre

The steel of Damascus blades, which were first encountered by the Crusaders when fighting against Muslims, had features not found in European steels — a characteristic wavy banding pattern known as damask, extraordinary mechanical properties, and an exceptionally sharp cutting edge. Here we use high-resolution transmission electron microscopy to examine a sample of Damascus sabre steel from the seventeenth century and find that it contains carbon nanotubes as well as cementite nanowires. This microstructure may offer insight into the beautiful banding pattern of the ultrahigh-carbon steel created from an ancient recipe that was lost long ago.

It is believed that Damascus blades were forged directly from small cakes of steel (named '*wootz*') produced in ancient India. A sophisticated thermomechanical treatment of forging and annealing was applied to these cakes to refine the steel to its exceptional quality. However, European bladesmiths were unable to replicate the process, and its secret was lost at about the end of the eighteenth century. It was unclear how medieval blacksmiths would have overcome the inherent brittleness of the plates of cementite (Fe_3C, a mineral known as cohenite) that form in steel with a carbon content of 1–2 wt%, as well as how the steel's characteristic banding could have arisen from these plates.



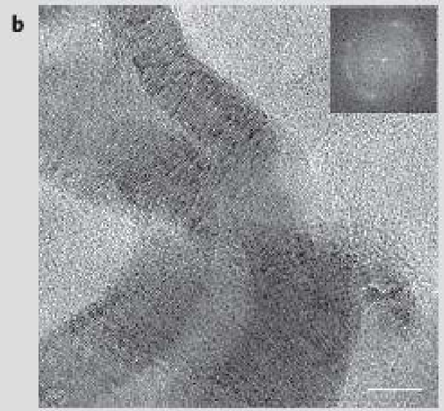


Figure 1 | High-resolution transmission electron microscopy images of carbon nanotubes in a genuine Damascus sabre after dissolution in hydrochloric acid. a, b, Multiwalled tubes with the characteristic layer distance $d \approx 0.34$ nm (ref. 12), as indicated by the Fourier transforms (see insets). Scale bars: 5 nm (**a**) and 10 nm (**b**). In **b**, the tubes are bent like a rope. **c**, Remnants of cementite nanowires encapsulated by carbon nanotubes, which prevent the wires from dissolving in acid. Scale bar, 5 nm. The fringe spacing of the wire is 0.635 nm, taken from the Fourier transform (inset), and is attributed to the (010) lattice planes of cementite.

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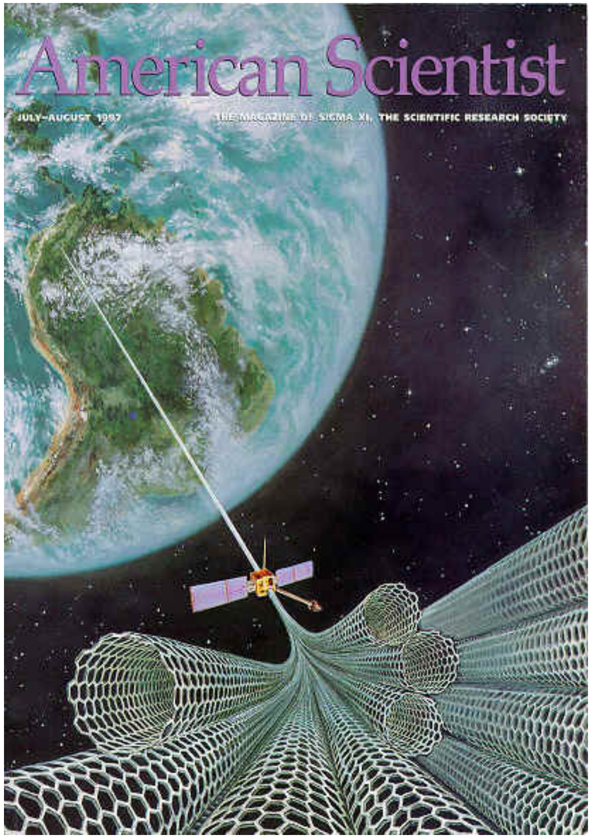
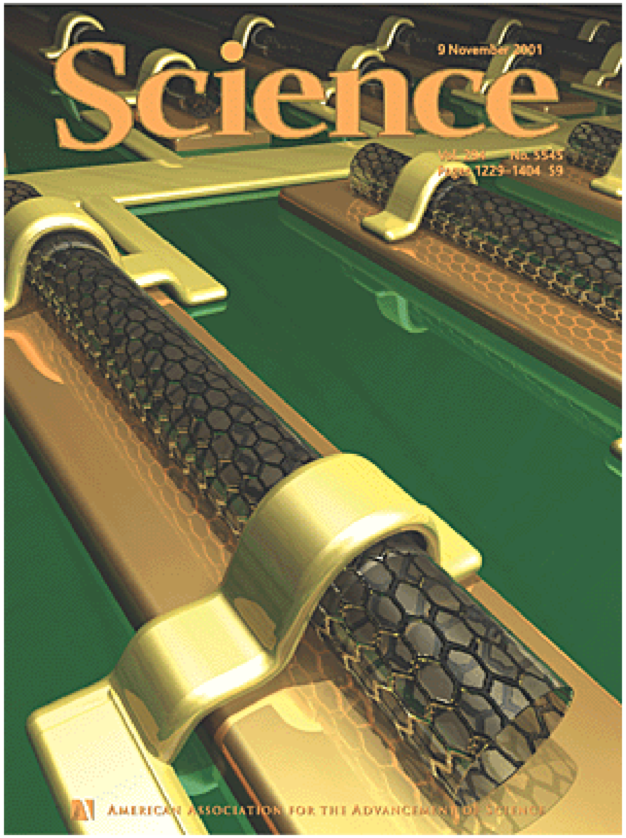
Reibold et al., Nature 444 (2006) 286

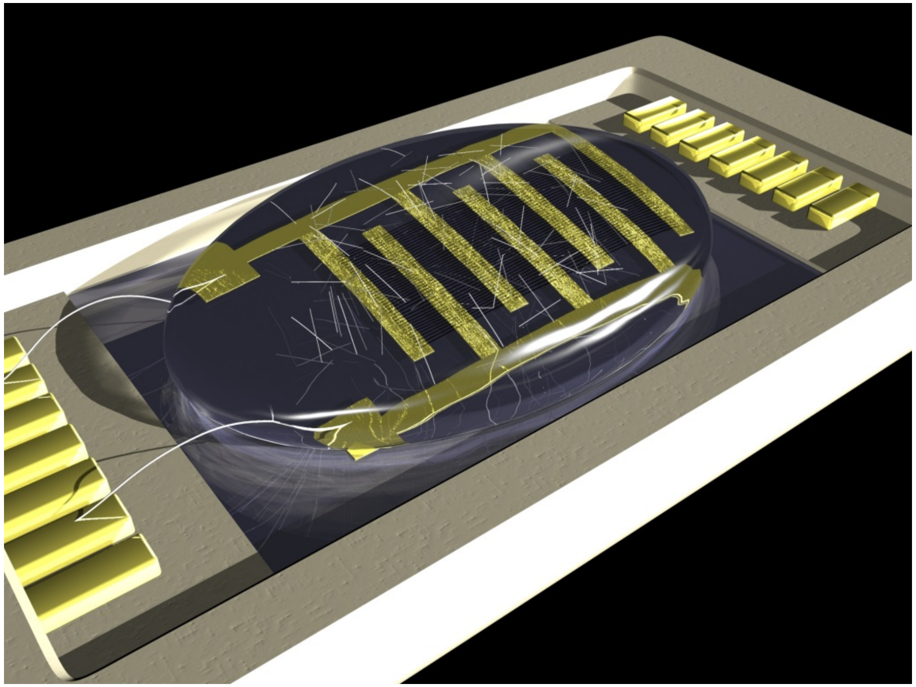
Early Visions



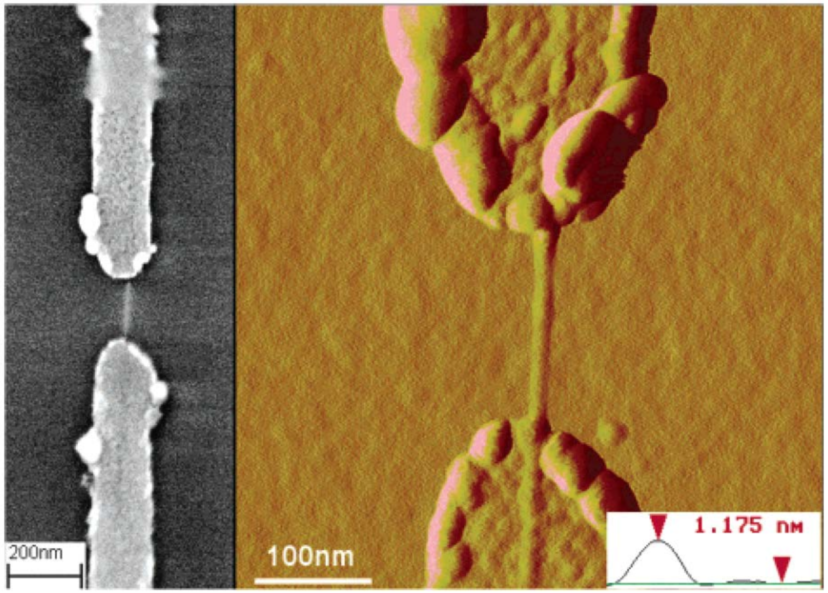


Early challenges

- Sorting of carbon nanotubes
- Integration of CNTs into device architectures

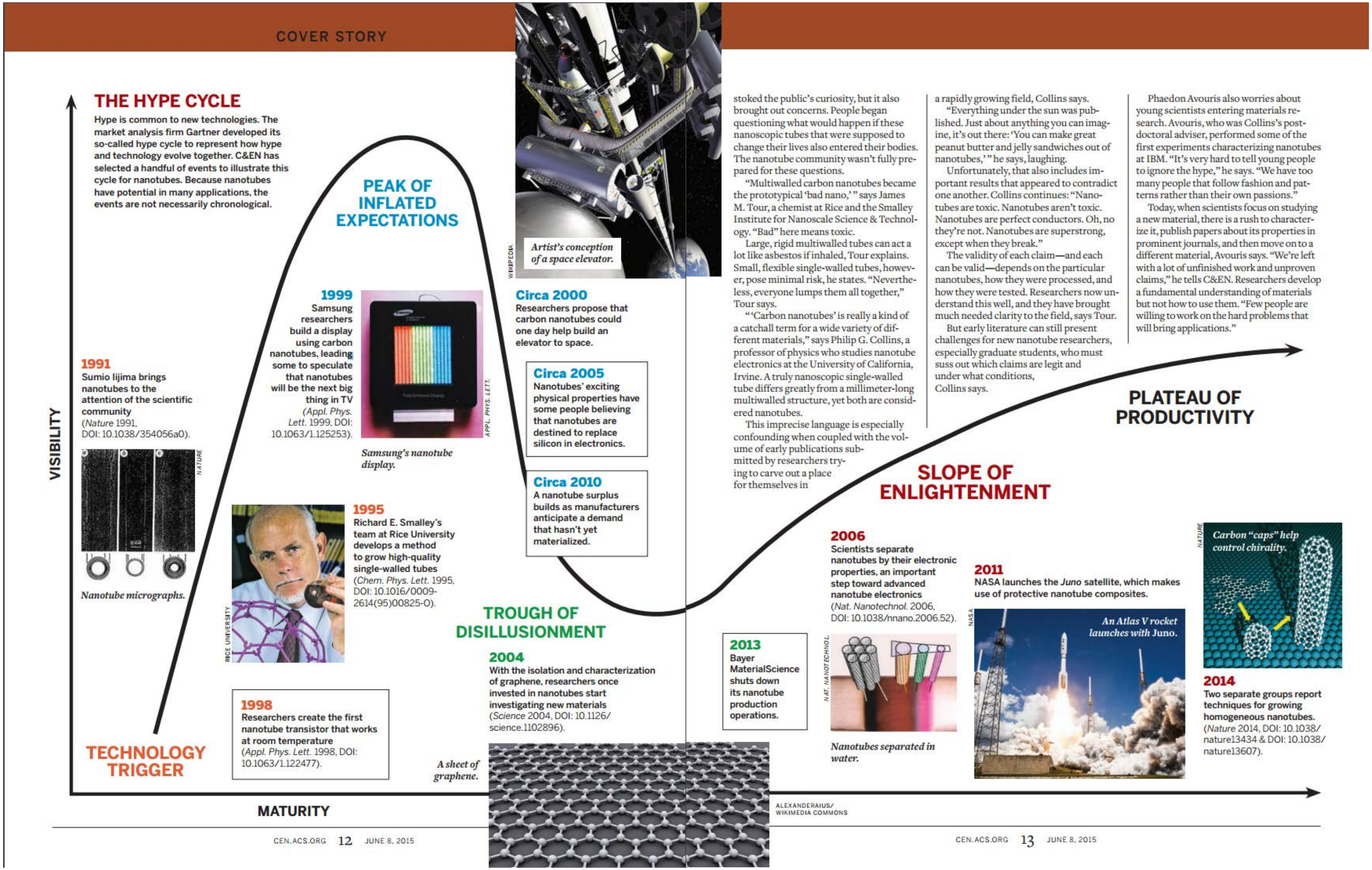


RK, F. Hennrich, H. von Löhneysen, M. M. Kappes
Science 301 (2003) 344-347



RK, F. Hennrich, H. B. Weber, M. M. Kappes, H. von Löhneysen, Nano Lett. 3 (2003) 1019-1023

Carbon Nanotube Hype Cycle



COVER STORY

THE HYPE CYCLE

Hype is common to new technologies. The market analysis firm Gartner developed its so-called hype cycle to represent how hype and technology evolve together. C&EN has selected a handful of events to illustrate this cycle for nanotubes. Because nanotubes have potential in many applications, the events are not necessarily chronological.

1991
Sumio Iijima brings nanotubes to the attention of the scientific community (*Nature* 1991, DOI: 10.1038/354056a0).

Nanotube micrographs.

1995
Richard E. Smalley's team at Rice University develops a method to grow high-quality single-walled tubes (*Chem. Phys. Lett.* 1995, DOI: 10.1016/0009-2614(95)00825-O).

1998
Researchers create the first nanotube transistor that works at room temperature (*Appl. Phys. Lett.* 1998, DOI: 10.1063/1.122477).

1999
Samsung researchers build a display using carbon nanotubes, leading some to speculate that nanotubes will be the next big thing in TV (*Appl. Phys. Lett.* 1999, DOI: 10.1063/1.125253).

Samsung's nanotube display.

Artist's conception of a space elevator.

Circa 2000
Researchers propose that carbon nanotubes could one day help build an elevator to space.

Circa 2005
Nanotubes' exciting physical properties have some people believing that nanotubes are destined to replace silicon in electronics.

Circa 2010
A nanotube surplus builds as manufacturers anticipate a demand that hasn't yet materialized.

2004
With the isolation and characterization of graphene, researchers once invested in nanotubes start investigating new materials (*Science* 2004, DOI: 10.1126/science.1102896).

A sheet of graphene.

stoked the public's curiosity, but it also brought out concerns. People began questioning what would happen if these nanoscopic tubes that were supposed to change their lives also entered their bodies. The nanotube community wasn't fully prepared for these questions.

"Multiwalled carbon nanotubes became the prototypical 'bad nano,'" says James M. Tour, a chemist at Rice and the Smalley Institute for Nanoscale Science & Technology. "Bad" here means toxic.

Large, rigid multiwalled tubes can act a lot like asbestos if inhaled, Tour explains. Small, flexible single-walled tubes, however, pose minimal risk, he states. "Nevertheless, everyone lumps them all together," Tour says.

"'Carbon nanotubes' is really a kind of a catchall term for a wide variety of different materials," says Philip G. Collins, a professor of physics who studies nanotube electronics at the University of California, Irvine. A truly nanoscopic single-walled tube differs greatly from a millimeter-long multiwalled structure, yet both are considered nanotubes.

This imprecise language is especially confounding when coupled with the volume of early publications submitted by researchers trying to carve out a place for themselves in a rapidly growing field, Collins says.

"Everything under the sun was published. Just about anything you can imagine, it's out there: 'You can make great peanut butter and jelly sandwiches out of nanotubes,'" he says, laughing.

Unfortunately, that also includes important results that appeared to contradict one another. Collins continues: "Nanotubes are toxic. Nanotubes aren't toxic. Nanotubes are perfect conductors. Oh, no they're not. Nanotubes are superstrong, except when they break."

The validity of each claim—and each can be valid—depends on the particular nanotubes, how they were processed, and how they were tested. Researchers now understand this well, and they have brought much needed clarity to the field, says Tour.

But early literature can still present challenges for new nanotube researchers, especially graduate students, who must suss out which claims are legit and under what conditions, Collins says.

Phaedon Avouris also worries about young scientists entering materials research. Avouris, who was Collins's postdoctoral adviser, performed some of the first experiments characterizing nanotubes at IBM. "It's very hard to tell young people to ignore the hype," he says. "We have too many people that follow fashion and patterns rather than their own passions."

Today, when scientists focus on studying a new material, there is a rush to characterize it, publish papers about its properties in prominent journals, and then move on to a different material, Avouris says. "We're left with a lot of unfinished work and unproven claims," he tells C&EN. Researchers develop a fundamental understanding of materials but not how to use them. "Few people are willing to work on the hard problems that will bring applications."

2006
Scientists separate nanotubes by their electronic properties, an important step toward advanced nanotube electronics (*Nat. Nanotechnol.* 2006, DOI: 10.1038/nnano.2006.52).

Nanotubes separated in water.

2013
Bayer MaterialScience shuts down its nanotube production operations.

2011
NASA launches the *Juno* satellite, which makes use of protective nanotube composites.

An Atlas V rocket launches with Juno.

Carbon "caps" help control chirality.

2014
Two separate groups report techniques for growing homogeneous nanotubes. (*Nature* 2014, DOI: 10.1038/nature13434 & DOI: 10.1038/nature13607).

Chemical & Engineering News 2015

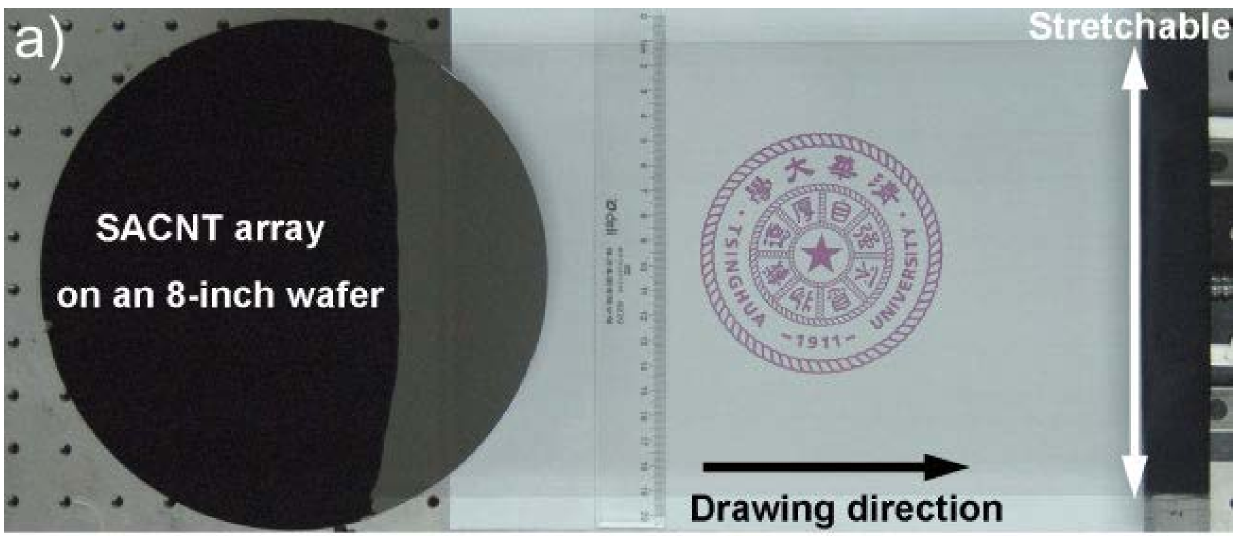
Market entry

Foxconn able to produce carbon nanotube touch panel sizes up to 10-inch

Ninelu Tu, Taipei; Joseph Tsai, DIGITIMES [Wednesday 22 May 2013]

Foxconn Electronics (Hon Hai Precision Industry) has successfully acquired the technology for carbon nanotube (CNT) touch panel production through cooperation between its subsidiary in Tianjin, China and an industrial R&D team of Tsinghua University in China. Mass producible panel sizes have also been expanded from only around 3.2-inch originally to a range between 1.52- to 10-inch, according to some market watchers.

Through the cooperation, the R&D team currently has about 107 patents for the technology, and Foxconn is currently able to manufacture 1.5 million CNT touch panel per month, the market watchers said.

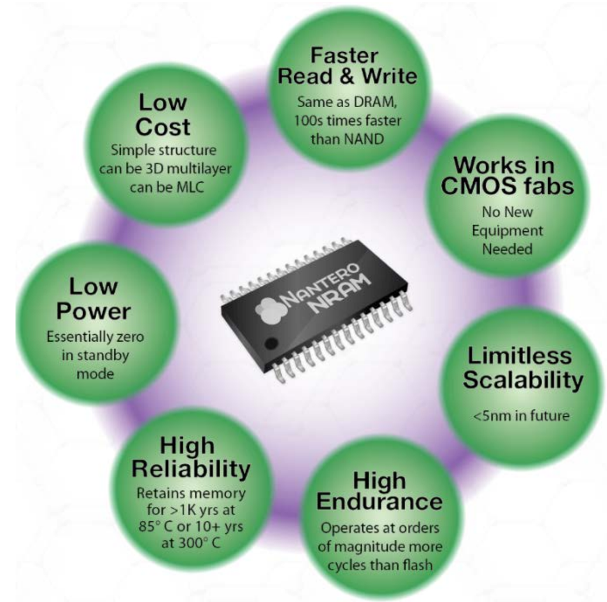


Feng et al., Adv. Funct. Mat. 20 (2010) 885

Market entry

PRESS RELEASE

31 August, 2016
Fujitsu Semiconductor Limited
Mie Fujitsu Semiconductor Limited
Nantero, Inc.

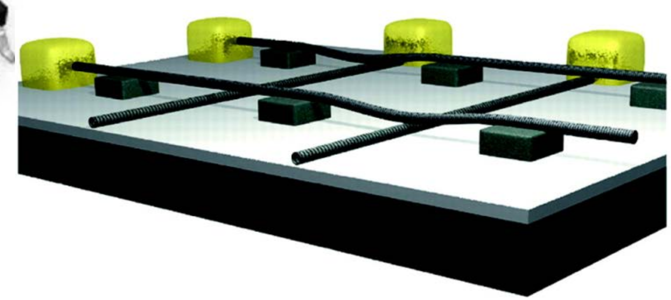


Fujitsu Semiconductor and Mie Fujitsu Semiconductor License Nantero's NRAM And Have Begun Developing Breakthrough Memory Products for Multiple Markets

Agreement covers joint development and licensing of ultrafast, ultrahigh-density NRAM, non-volatile RAM using carbon nanotubes

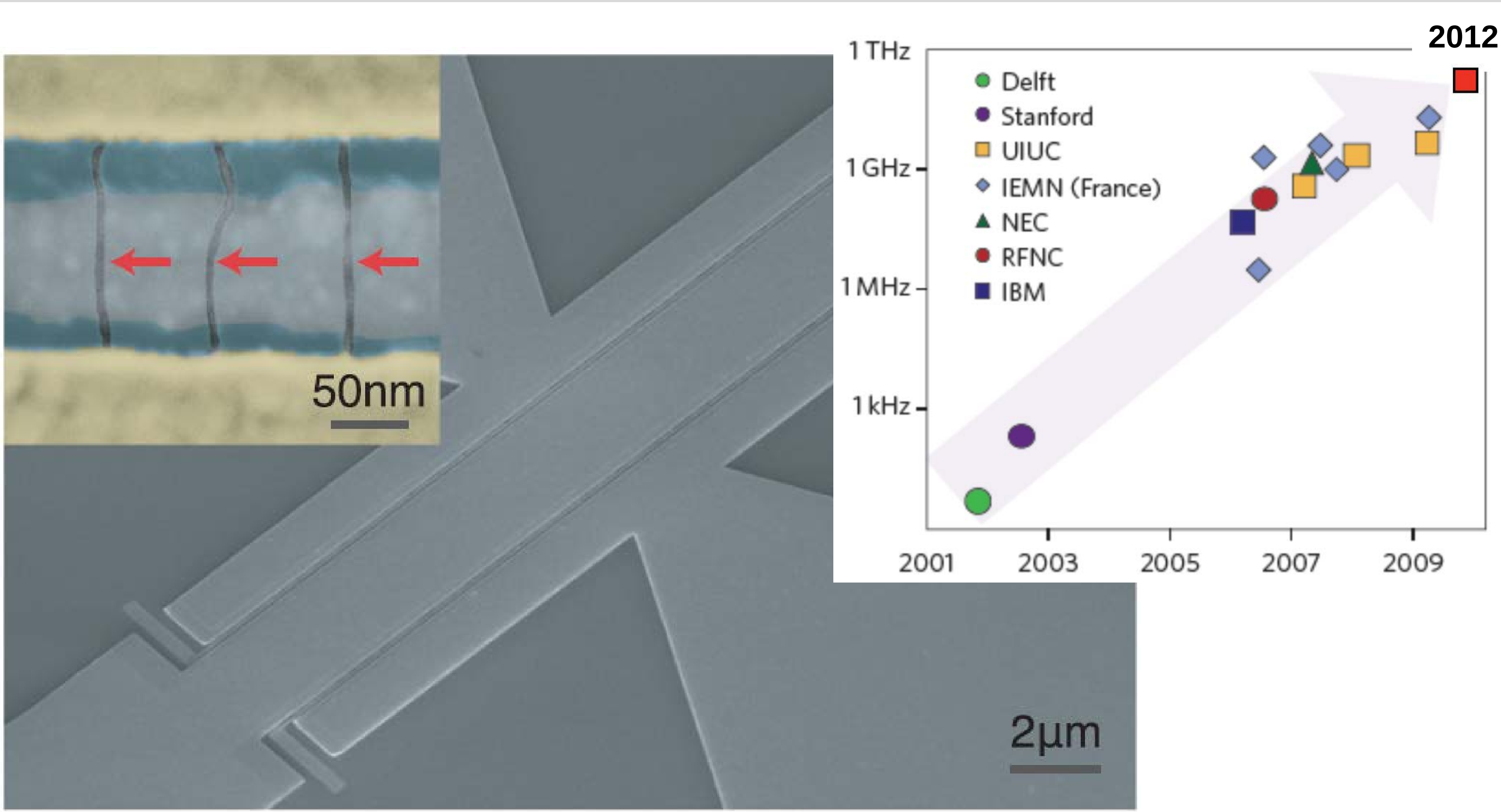
日本語

Yokohama, Japan and Woburn, Mass., USA, August 31, 2016 — Fujitsu Semiconductor Limited and Mie Fujitsu Semiconductor Limited today announced that they have reached an agreement with US-based Nantero, Inc. to license that company's technology for NRAM, non-volatile RAM using carbon nanotubes, and to conduct joint development towards releasing a product based on 55-nm process technology.



Rueckes et al., Science 7 (2000) 94

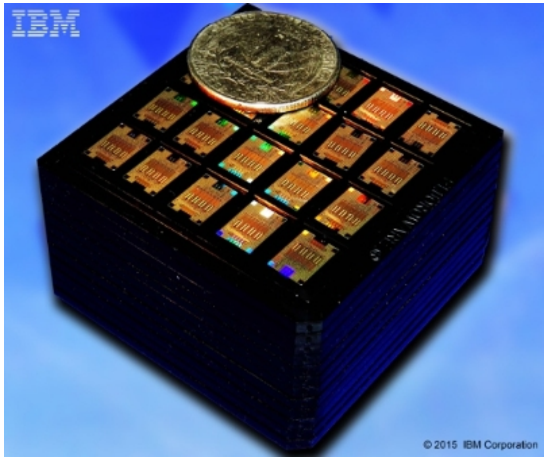
Carbon-nanotube high-frequency transistor



M. Steiner, M. Engel, Y.-M. Lin, Y. Wu, K. Jenkins, D.B. Farmer, N. Yoder, T.J. Seo, A.A. Green, M.C. Hersam, RK, P. Avouris, Appl. Phys. Lett 101 (2012) 053123.

US 8987705 B2, Carbon Nanotube Transistor Employing Embedded Electrodes, 24 Mar 2015.

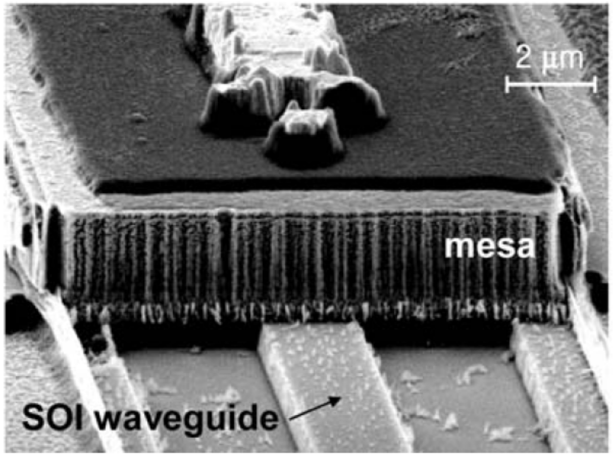
Current motivation

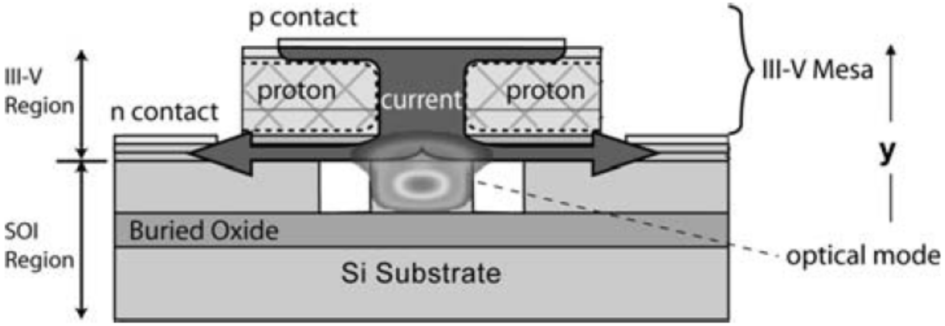


IBM Research 2015, May 13

Integrated wavelength multiplexed silicon photonics chip

"The lasers are brought in from off-chip in order to be modulated, but eventually we hope to incorporate III-V lasers right on the chip," Will Green.





Jones et al., J Mater Sci: Mater Electron (2009) 20:S3–S9

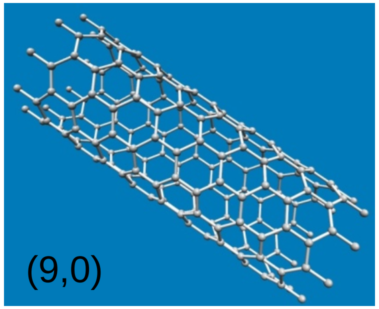
Our research interest

- **CNT sorting techniques (chromatography)**
- **CNT device integration (dielectrophoresis)**
- **Graphene-based devices (heterostructures)**
- **Photocurrent generation and solar cells**
- **Electroluminescence and incandescence**

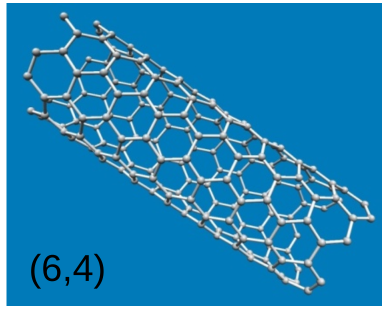
Senior scientists
Dr. Flavel
Dr. Danneau

- Waveguide-integrated carbon nanotube light sources
- Tailoring emission properties
- Non-classical light emission
- High-speed transducers

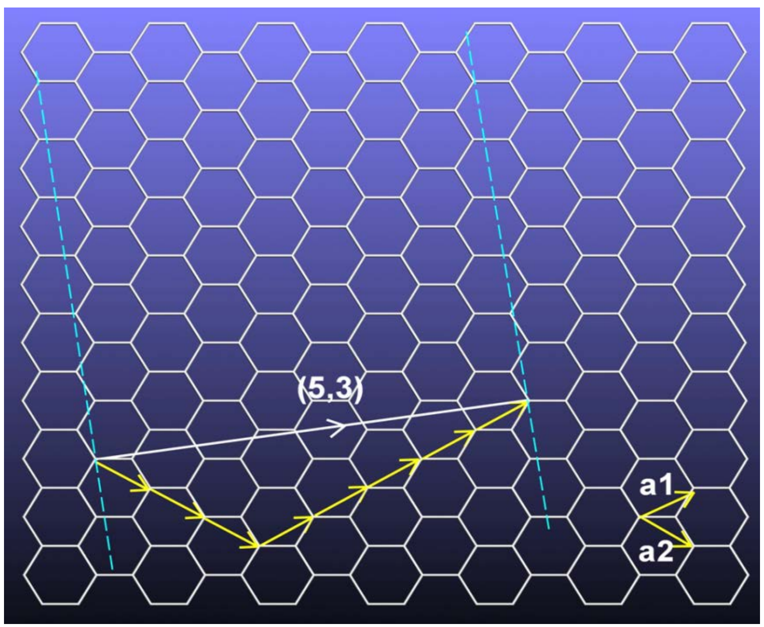
Structure of carbon nanotubes



metallic



semiconducting



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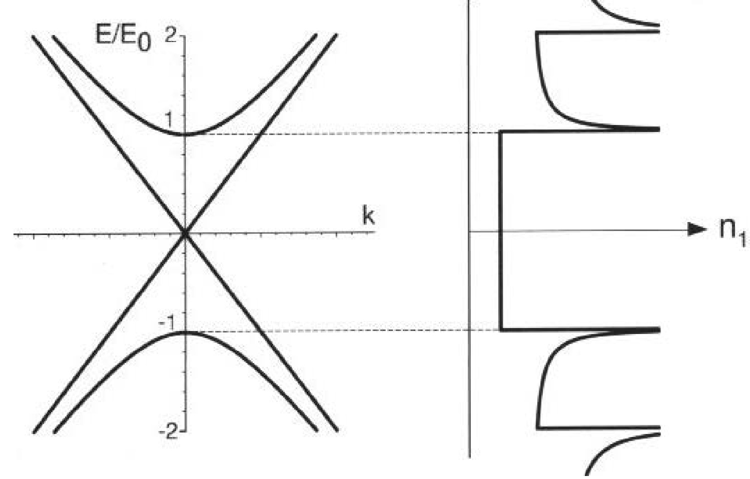
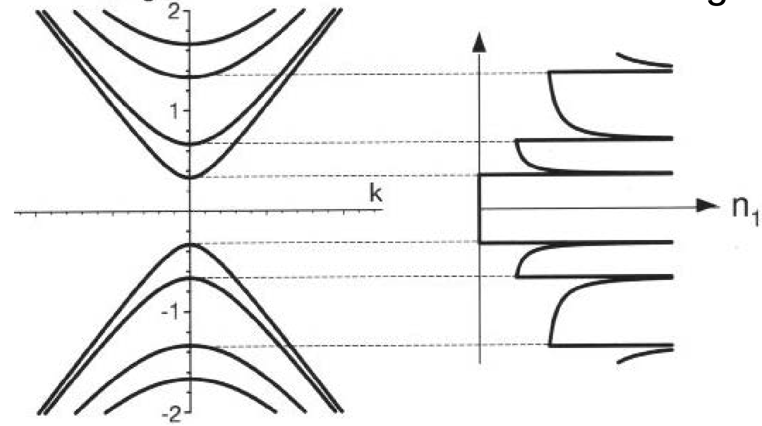
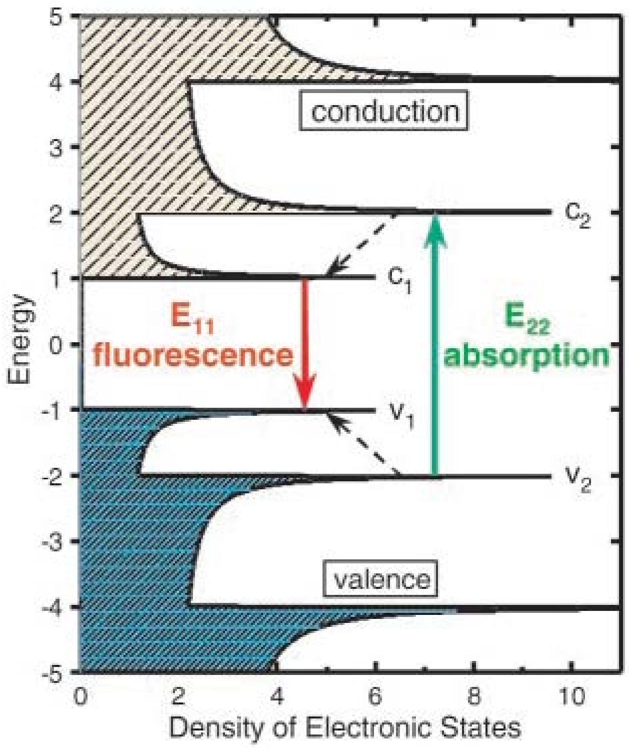
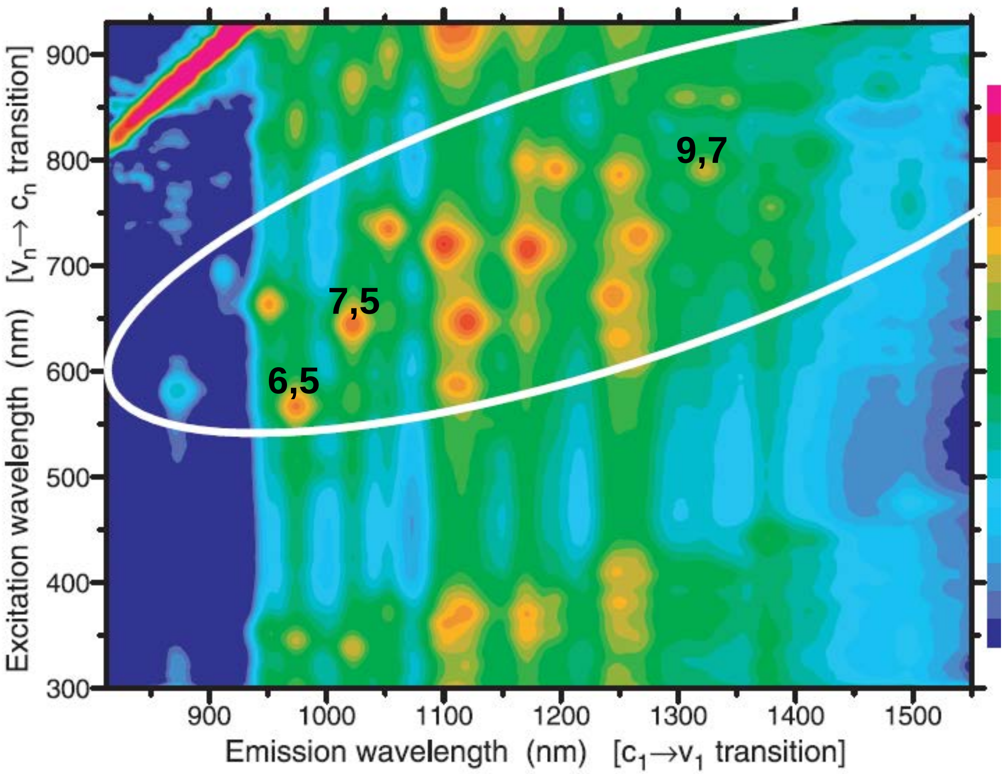


semiconducting



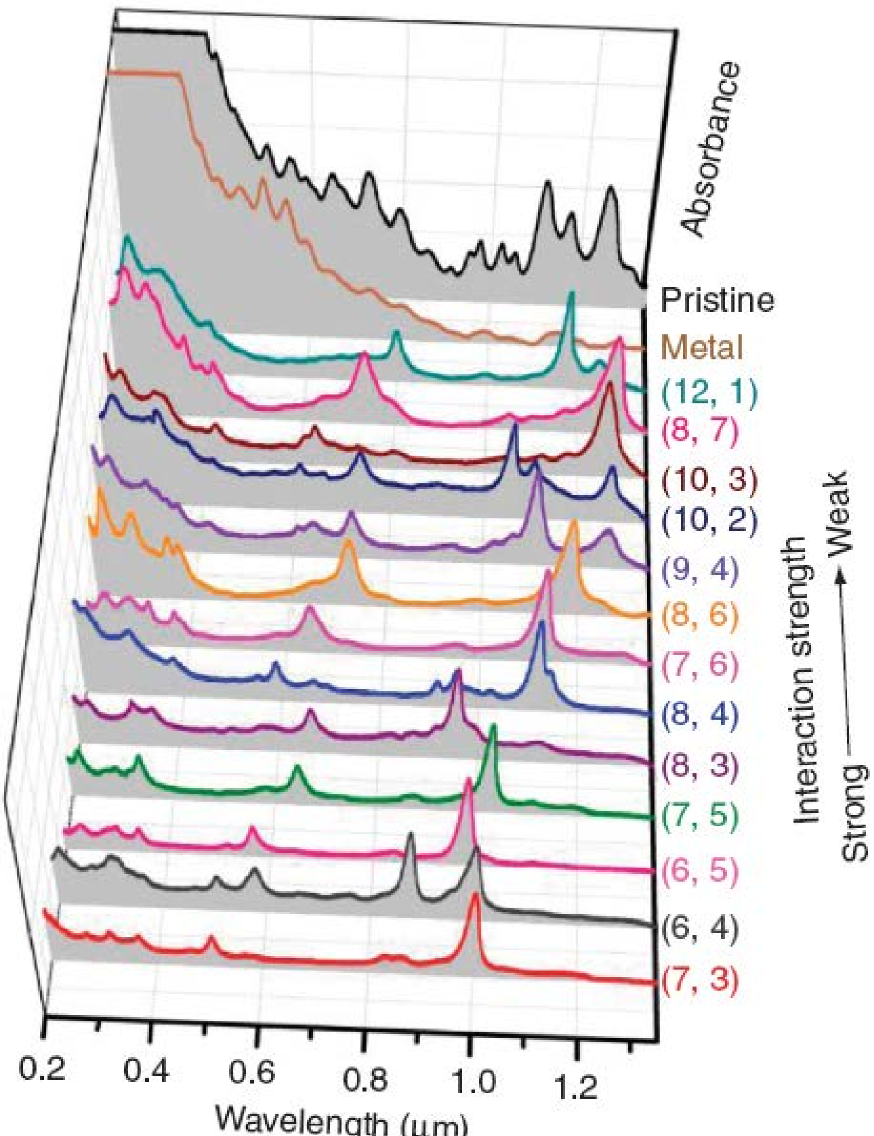
Fluorescence of semiconducting carbon nanotubes





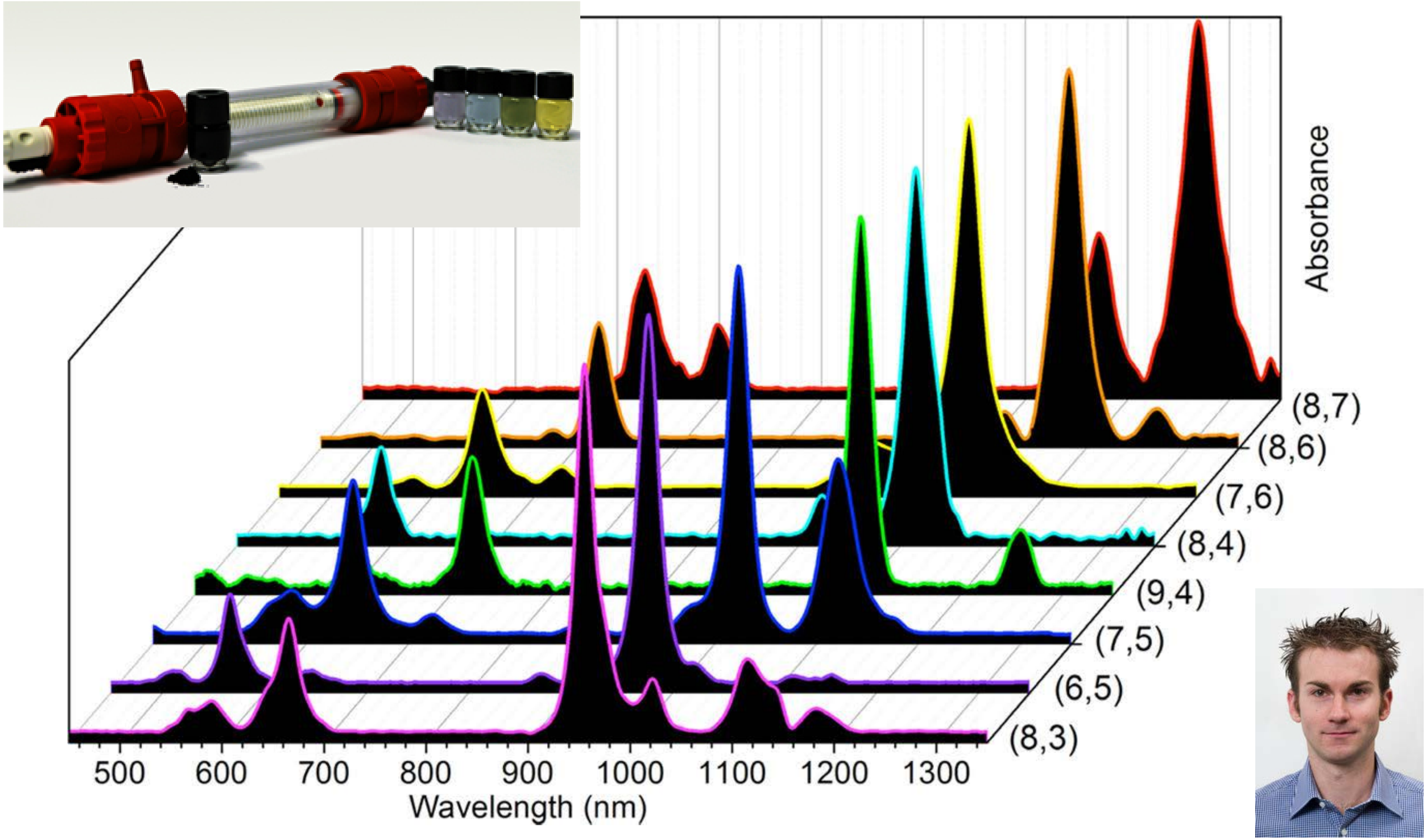
Bachilo et al., Science 298 (2002) 2361

Nanotubes have color !



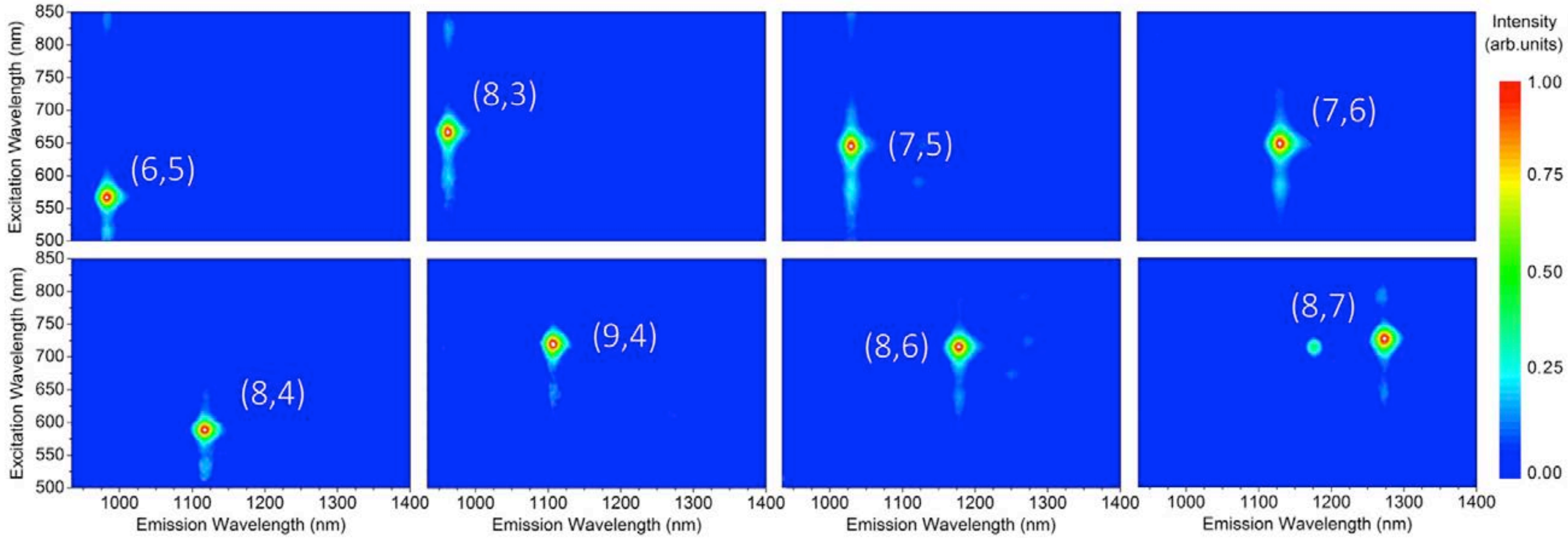
Liu, Nature Comm. 2011

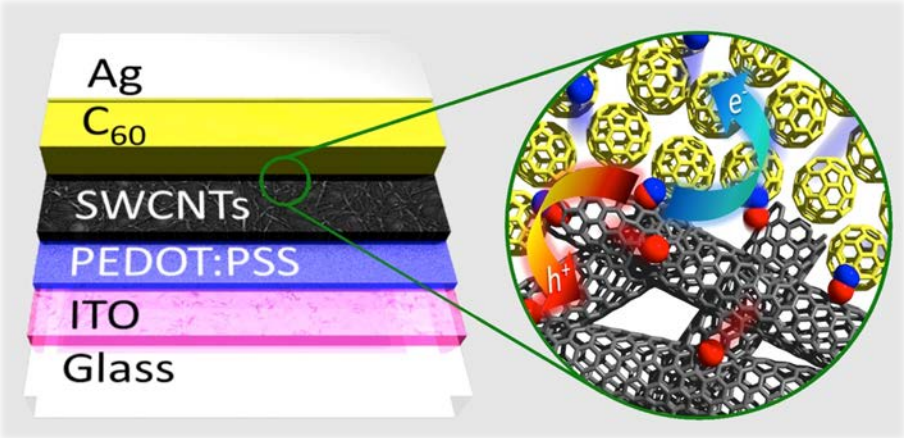
Aqueous dispersions from gel-permeation chromatography



B.S. Flavel et al., ACS Nano 8, 1817 (2014), ACS Nano 7, 3557 (2013)

Carbon nanotube solar cell project

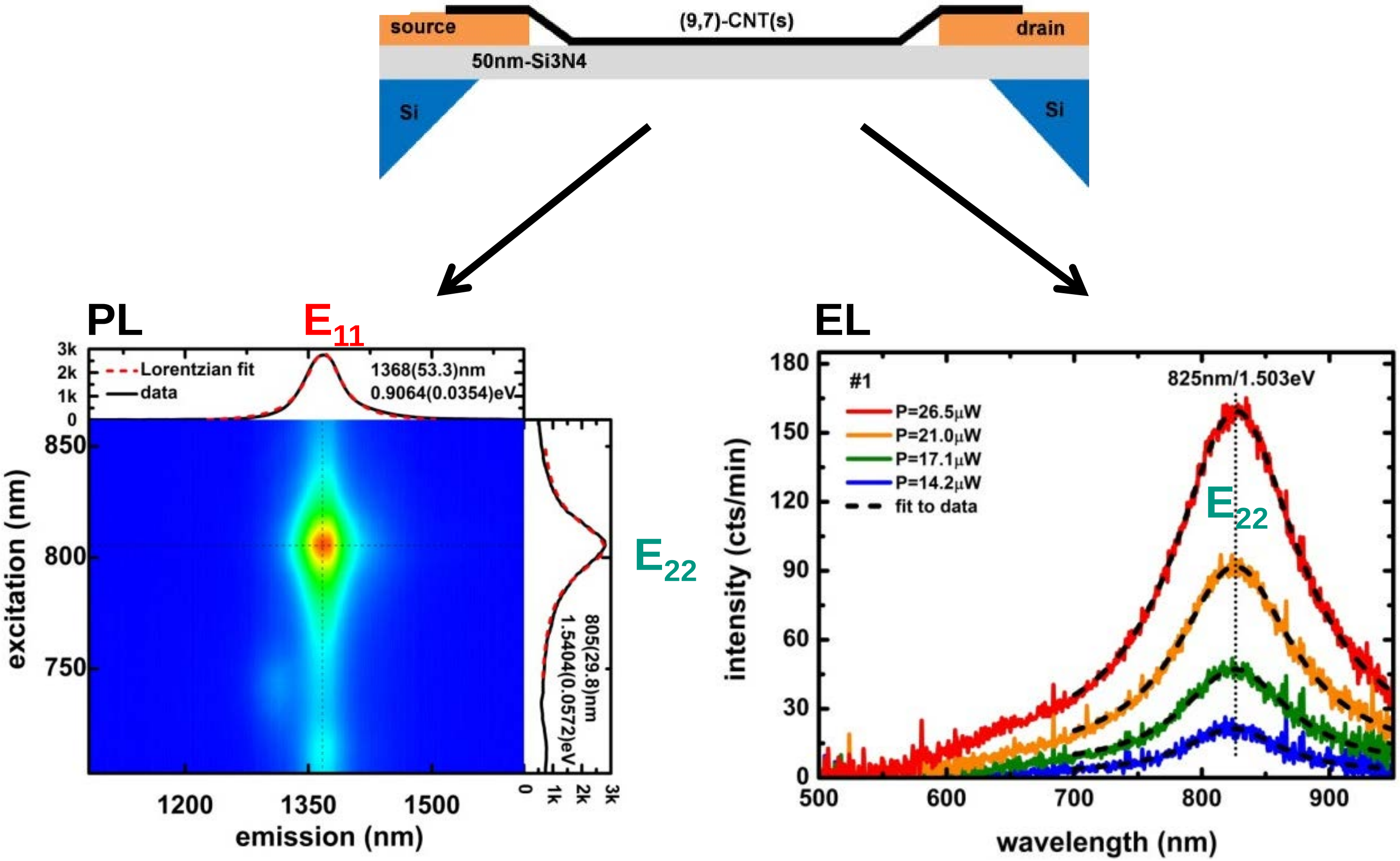




K.E. Moore, M. Pfohl, M.M. Kappes, R. Krupke, B.S. **Flavel** et al., ACS Nano 8 (2014) 6756.
K.E. Moore, M. Pfohl, D.D. Tune, M.M. Kappes, R. Krupke, B.S. **Flavel** et al., ACS Nano 4 (2015) 3849.

M. Pfohl, R. Krupke, B.S. **Flavel** et al., Adv. Energy Mater. 6 (2016) 1501345.

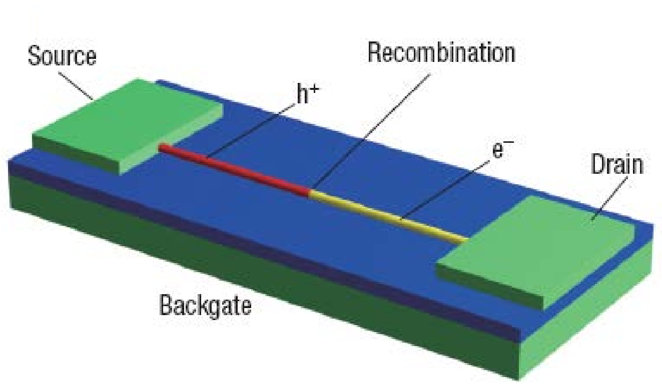
Electroluminescence versus Photoluminescence



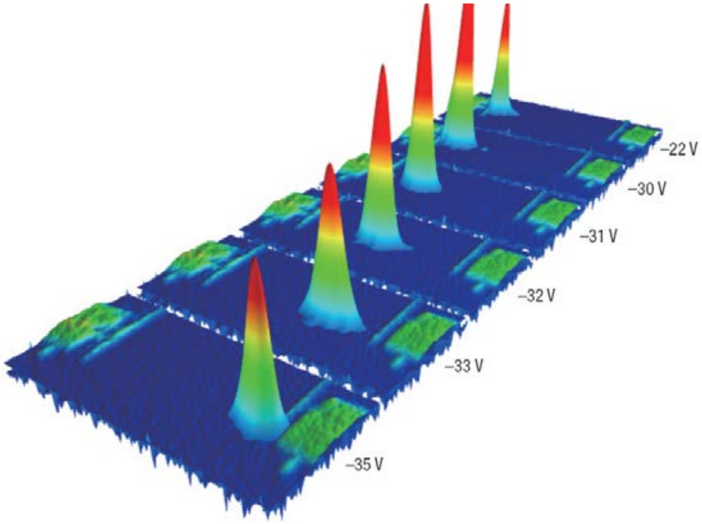
M.H.P. Pfeiffer, N. Stürzl, C.W. Marquardt, M. Engel, S. Dehm, F. Hennrich, M.M. Kappes, U. Lemmer, RK, Optics Express 19 (2011) A1184

Electroluminescence mechanism

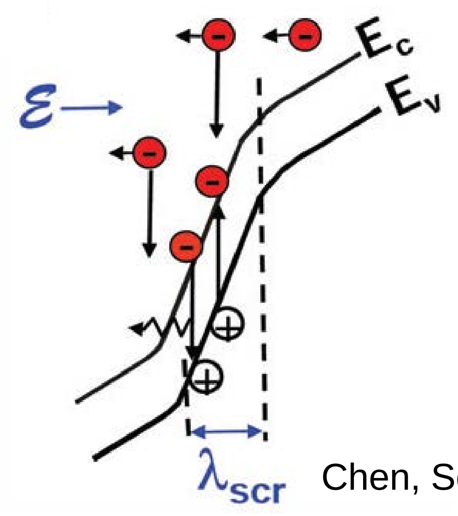
carrier recombination



Avouris, Freitag, Nat. Phot. 2008



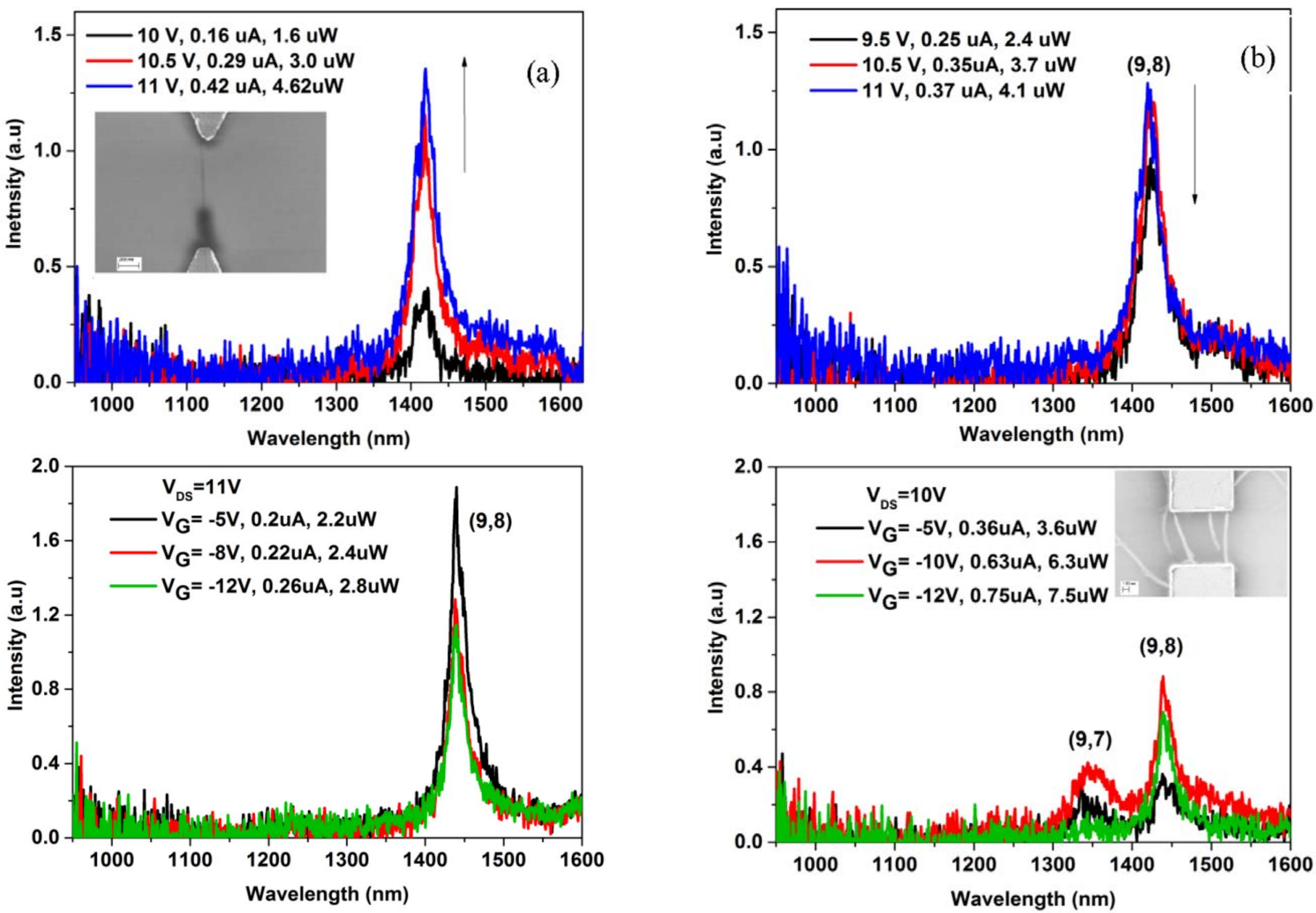
impact excitation



Chen, Science 2005

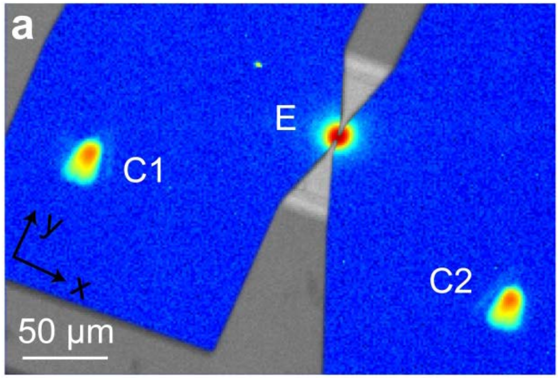
→ Electrically stimulated emission (electroluminescence) via impact excitation or carrier recombination.

Electroluminescence from (9,8)



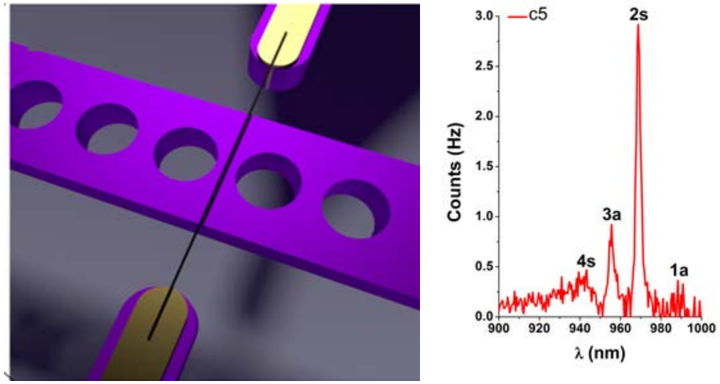
Carbon Nanotube Quantum Emitters

Waveguide-integrated CNT emitter



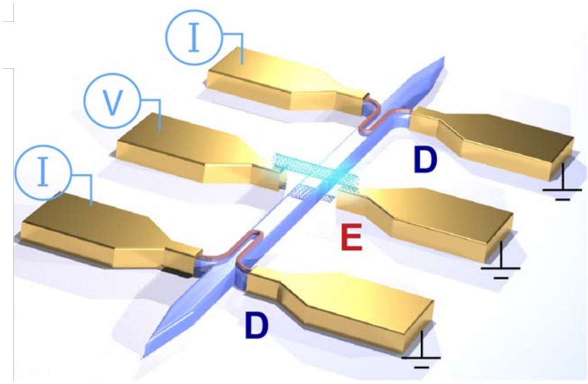
Pyatkov et al., Adv. Mat. 2014

Photonic crystal cavity enhancement



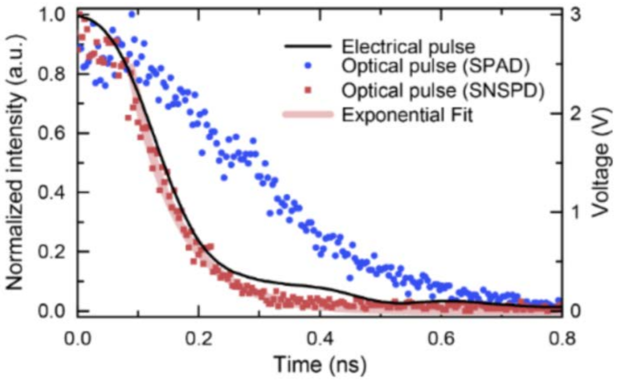
Pyatkov et al., Nature Photonics 2016

On-chip quantum photonic circuits



Khasminskaya et al., Nature Photonics 2016

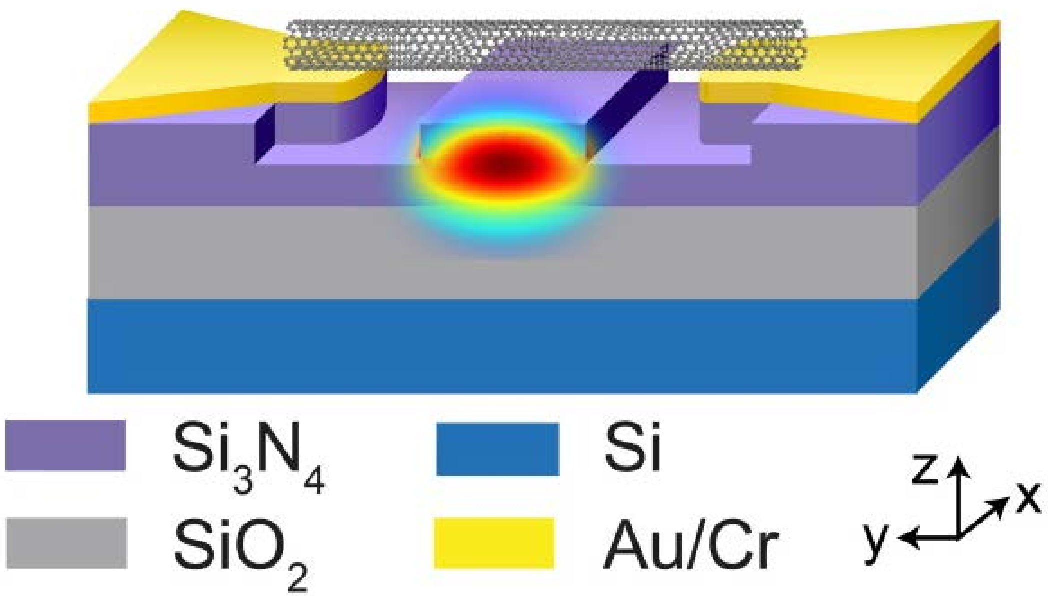
Ultra-fast response (<80ps)

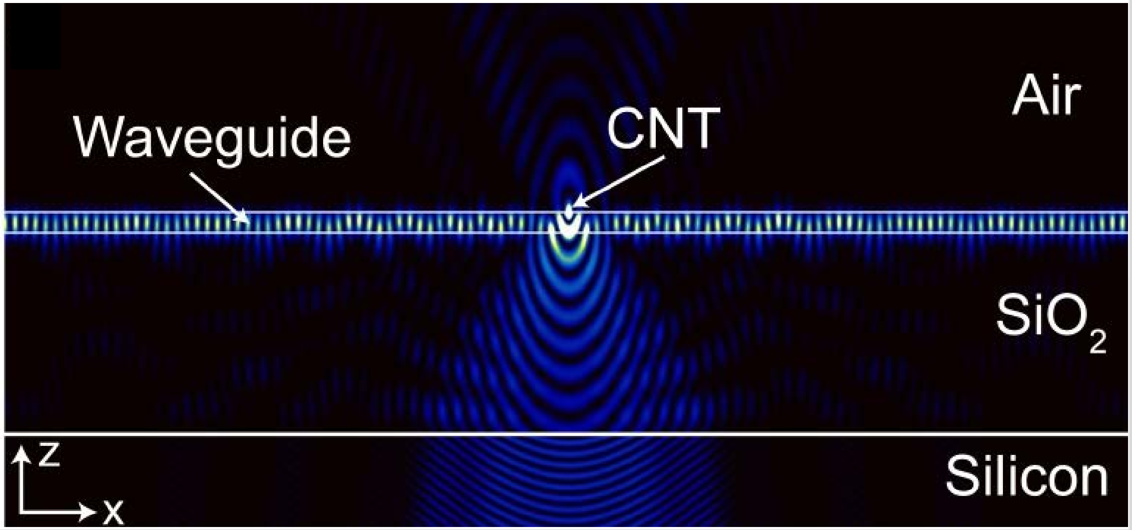


Pyatkov et al., Beilstein J. Nanotechnol. 2017

Waveguide-integrated carbon nanotube light sources

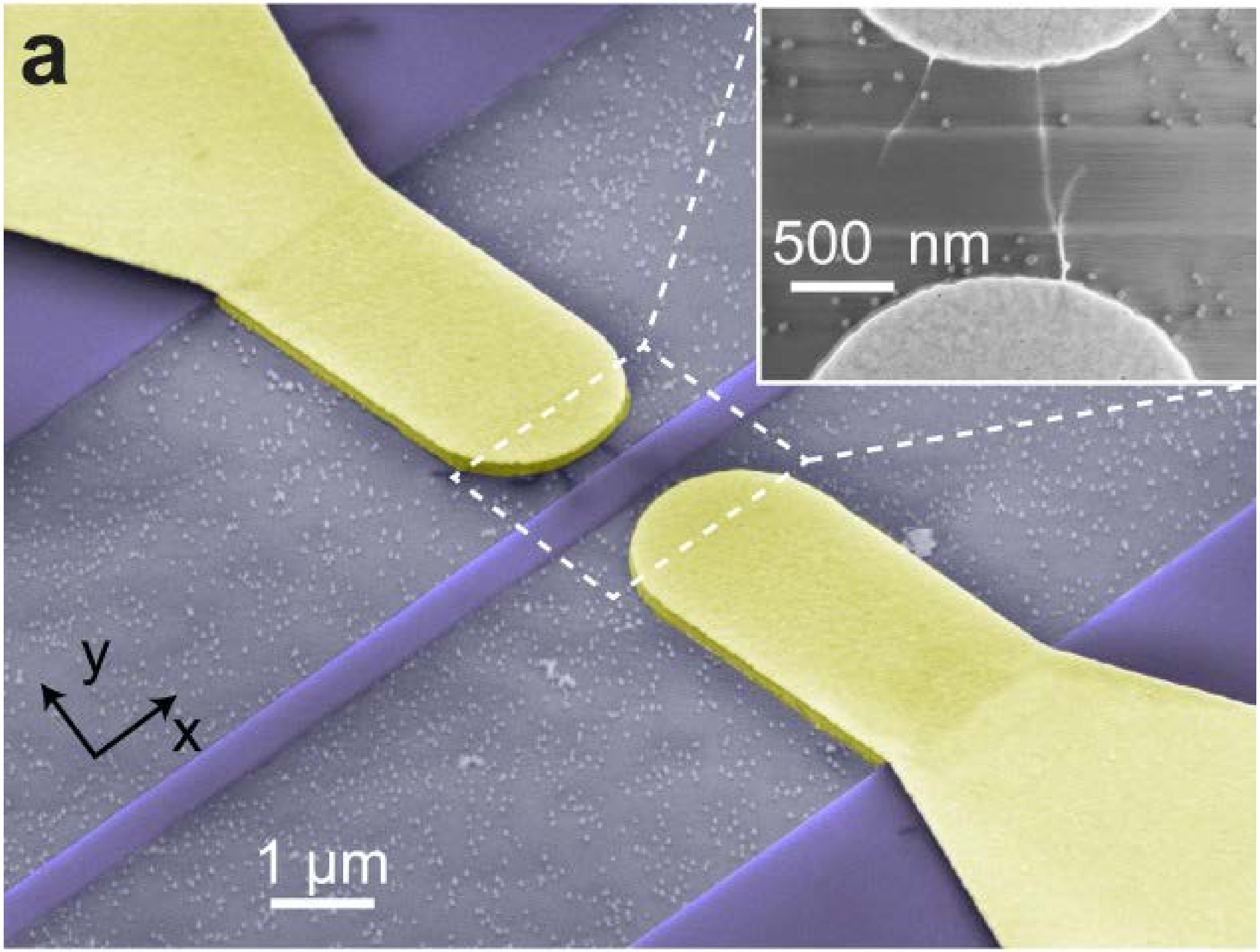
Concept of a waveguide-coupled electroluminescent nanotube





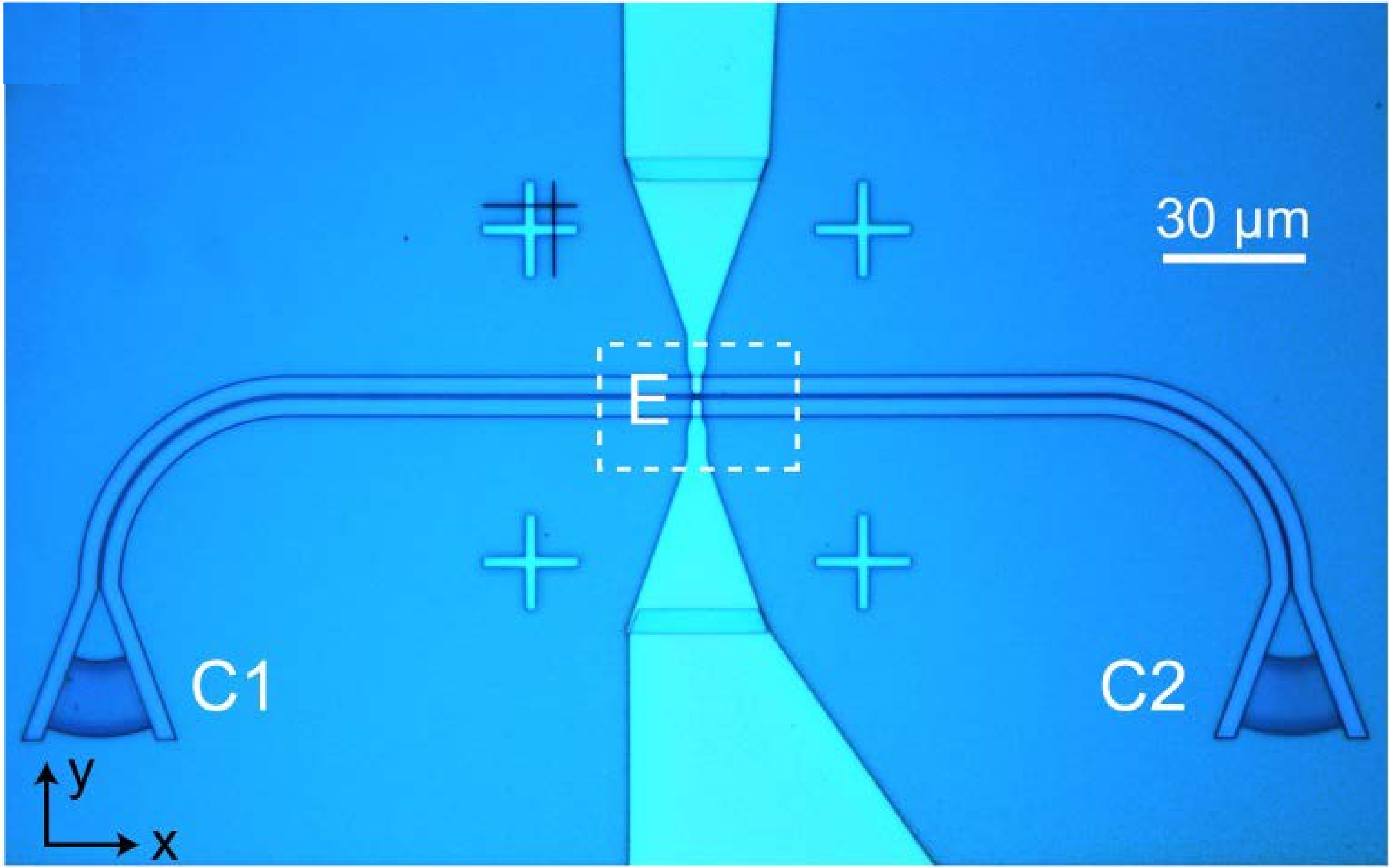
Simulations:
FDTD & MEEP

Waveguide-coupled carbon nanotube light emitter

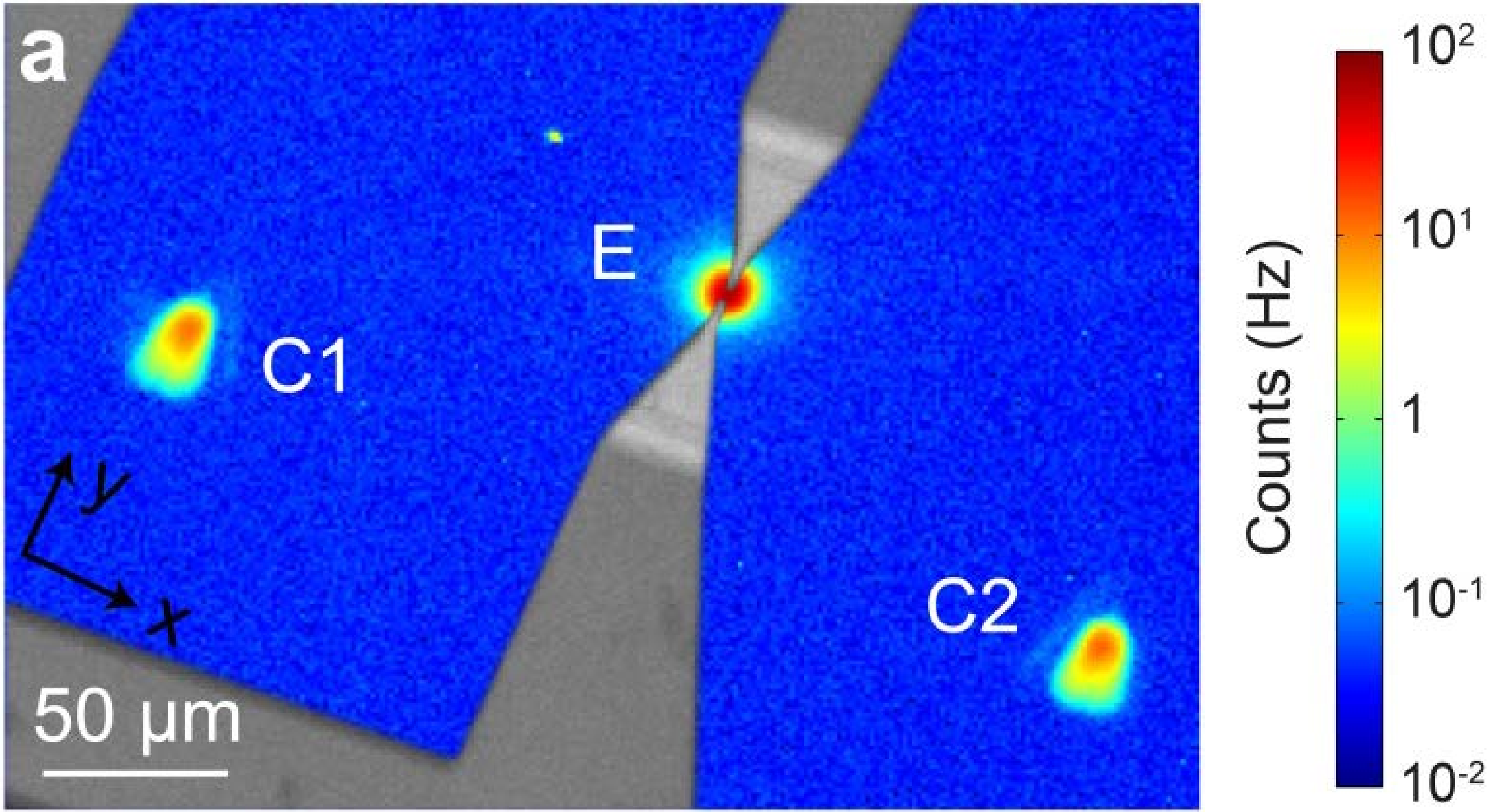


S. Khasmiskaya, F. Pyatkov, B. Flavel, W. H. Pernice, RK, Advanced Materials 26 (2014) 3465

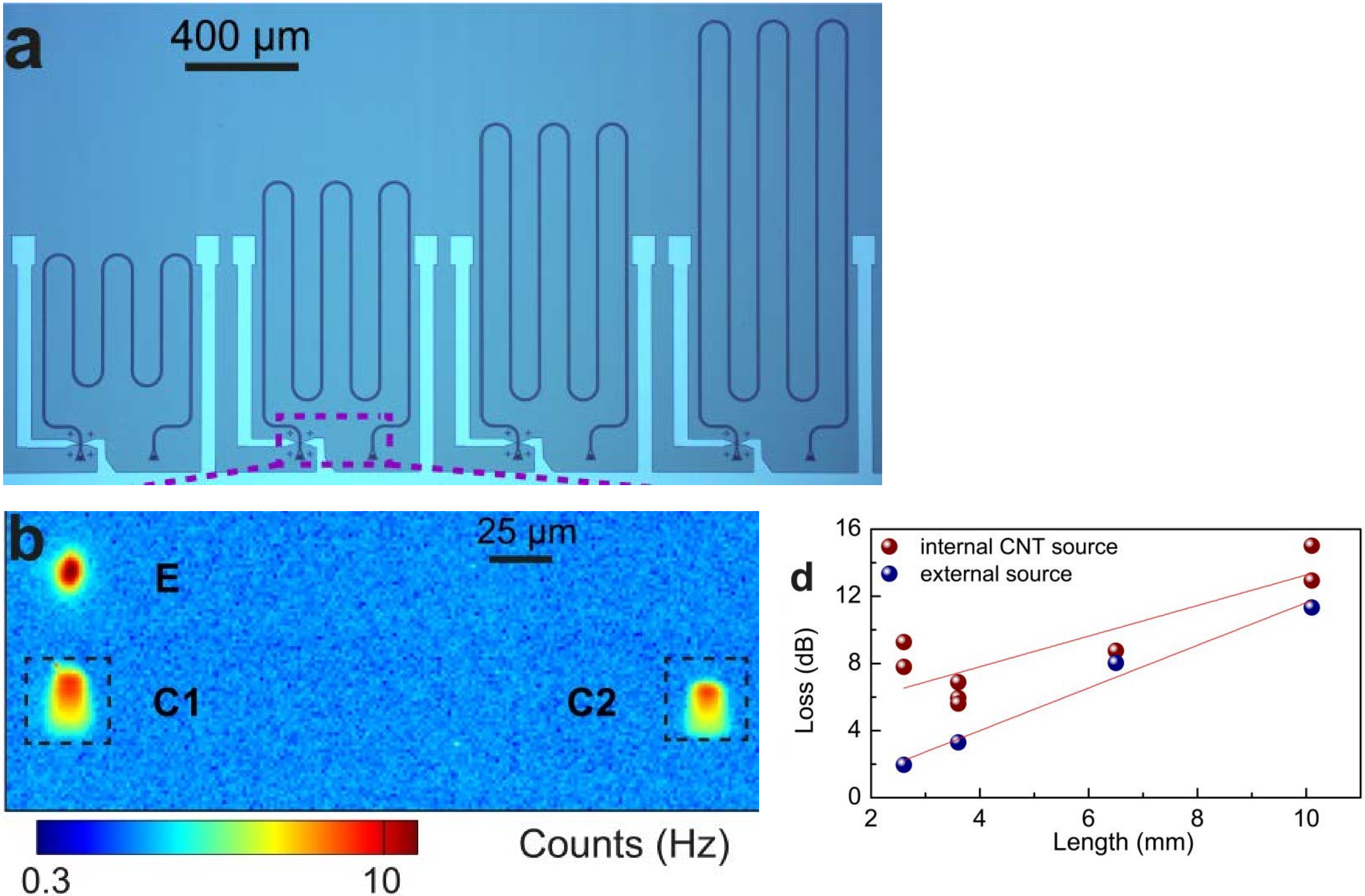
Waveguide-coupled carbon nanotube light emitter



Waveguide-coupled carbon nanotube light emitter

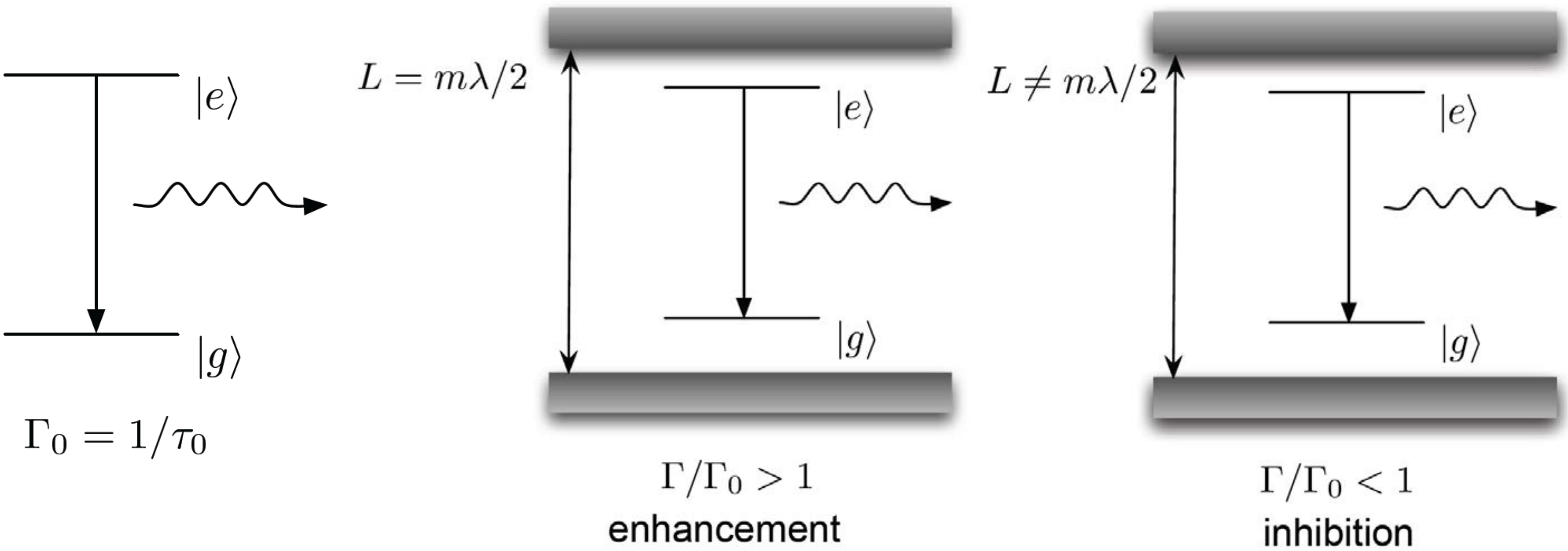


Propagation loss in extended waveguide structures



Tailoring emission properties

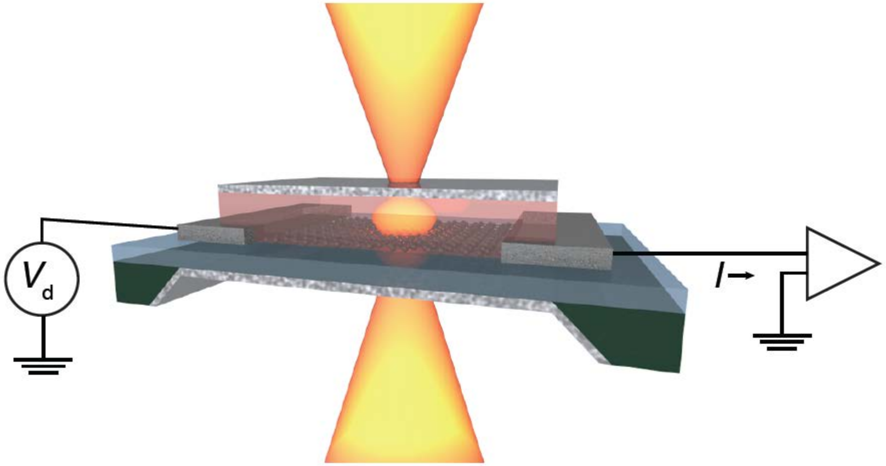
Principle of optical confinement

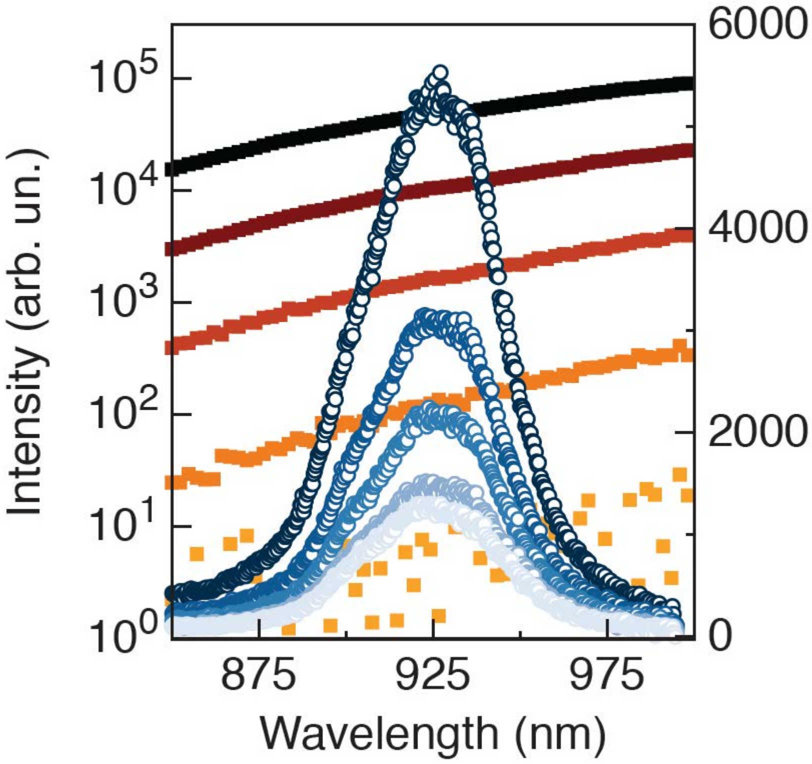


$$P = \frac{3}{4\pi^2}\left(\frac{\lambda}{n}\right)^3 \frac{Q}{V}$$

Purcell et al., Phys. Rev. (1946)
Kleppner, Phys. Rev. Lett. (1981)

Narrow-band thermal emission from graphene

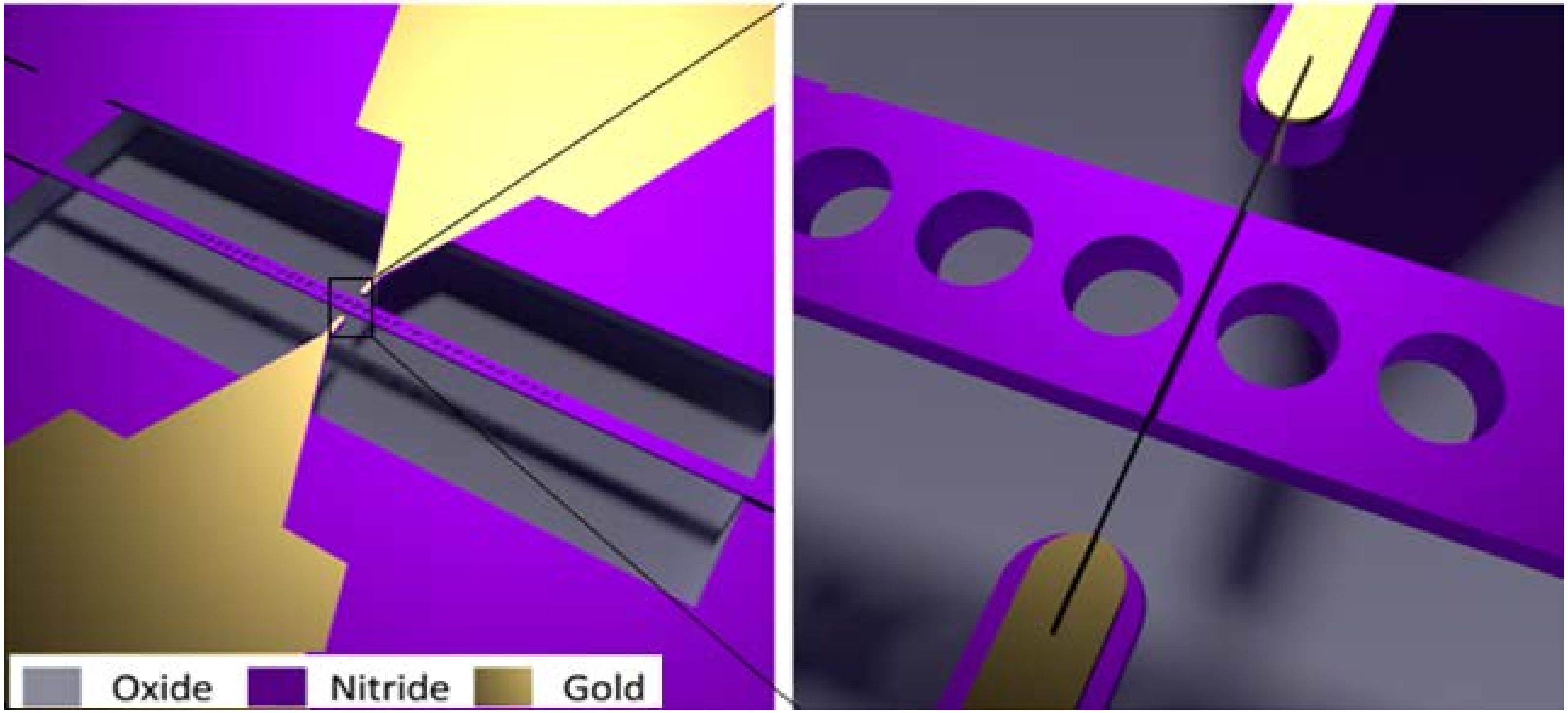




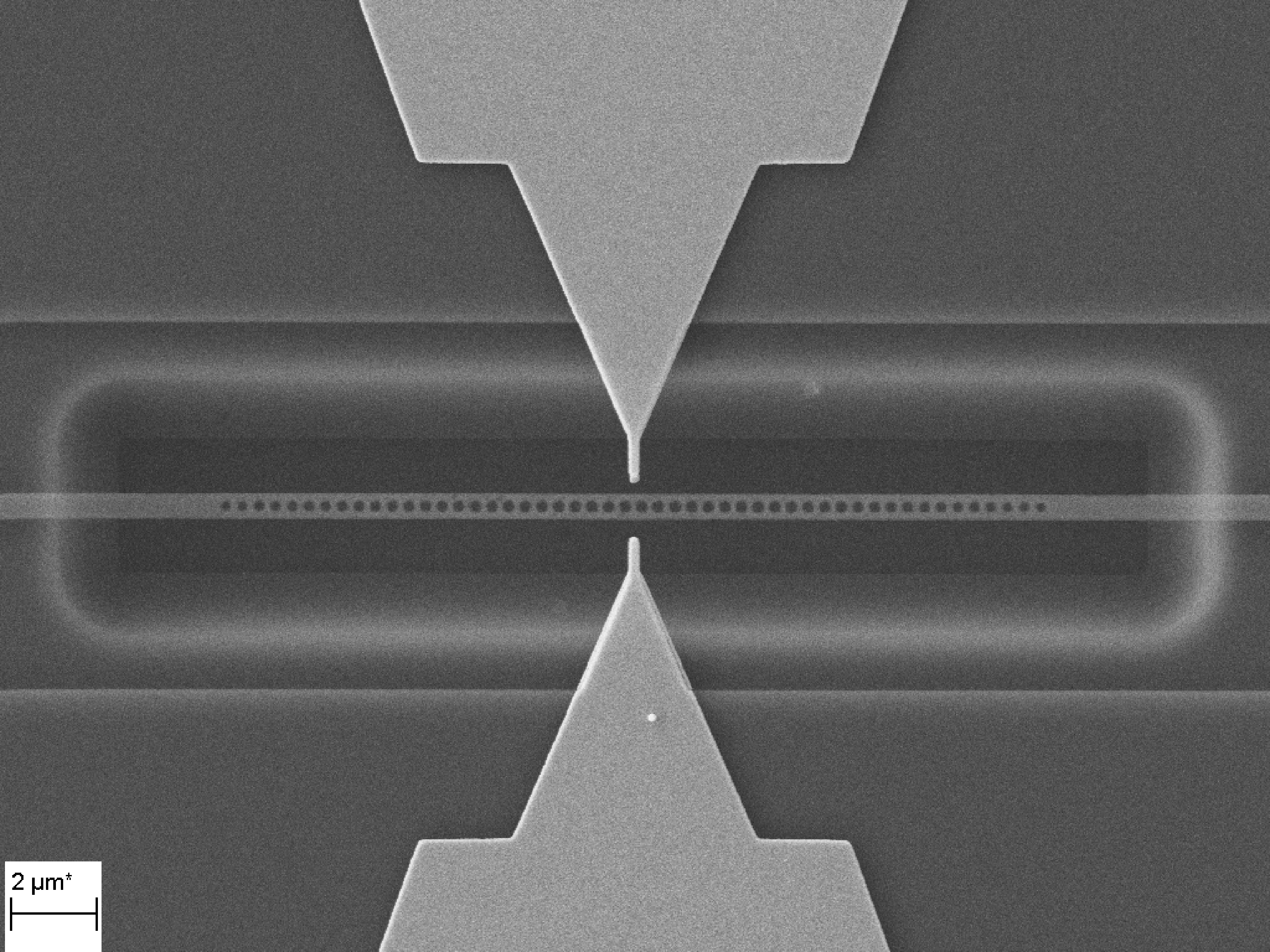
→ Spectral narrowing

M. Engel, M. Steiner, A. Lombardo, A.C. Ferrari, H.v. Löhneysen, P. Avouris, RK
Nature Communications 3 (2012) 906

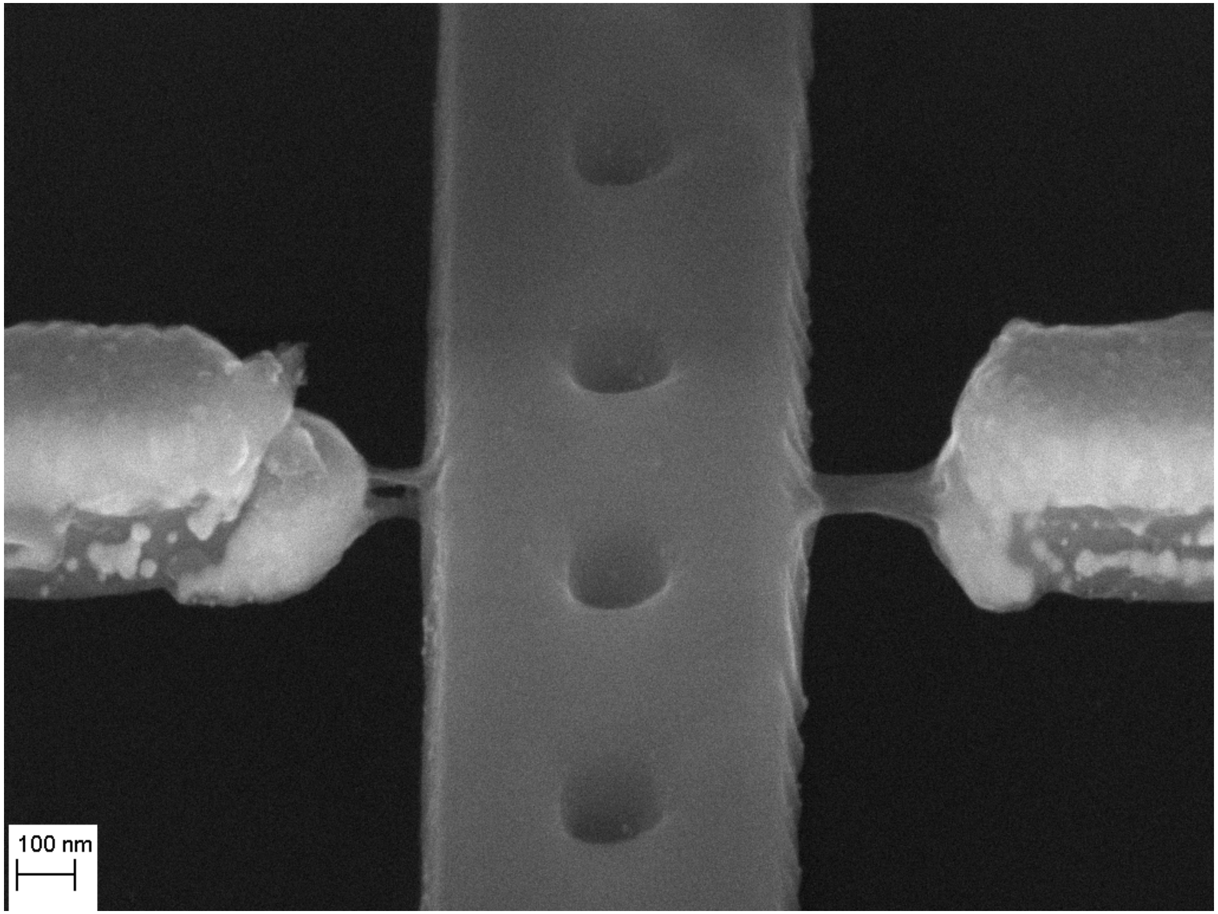
Tailoring emission with photonic crystal nanobeam cavities



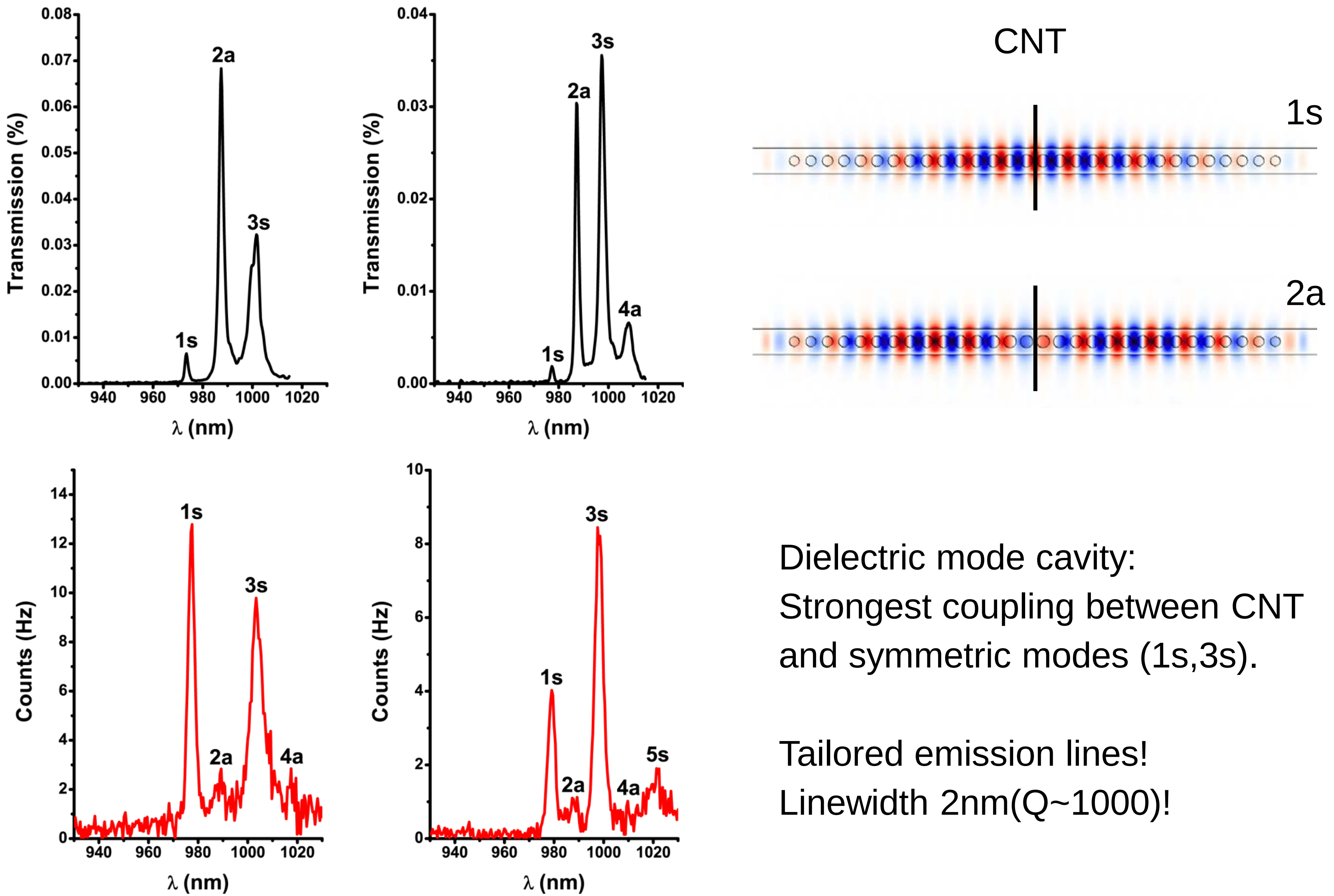
F. Pyatkov, V. Fütterling, S. Khasminskaya, B. Flavel, F. Hennrich, M.M. Kappes, W. Pernice, RK,
Nature Photonics 10 (2016) 420-427


2 µm*

Integration of CNTs into photonic crystal nanobeam cavities



Waveguided CNT-emission vs. transmission – dielectric mode

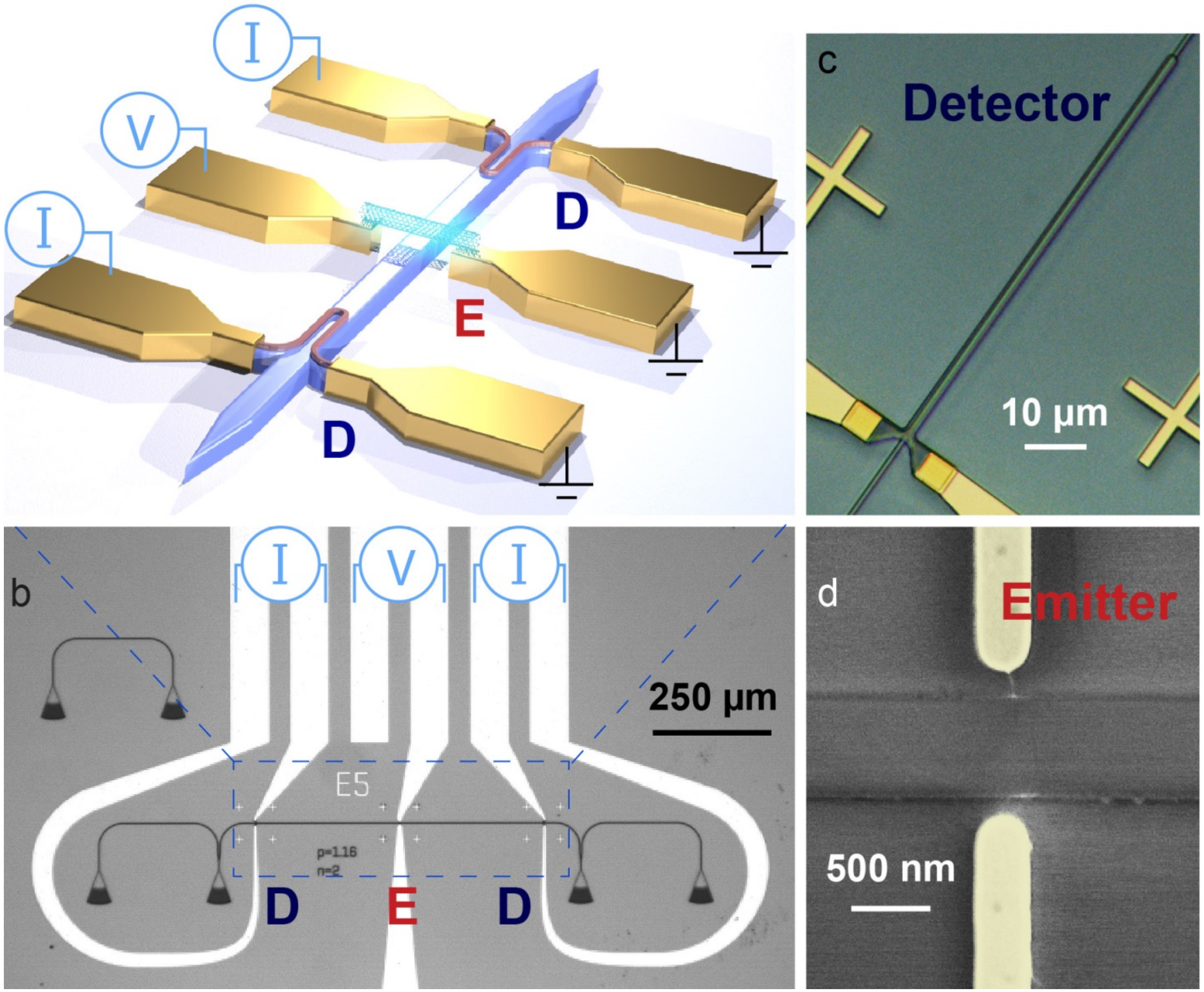


Dielectric mode cavity:
Strongest coupling between CNT and symmetric modes (1s,3s).

Tailored emission lines!
Linewidth 2nm(Q~1000)!

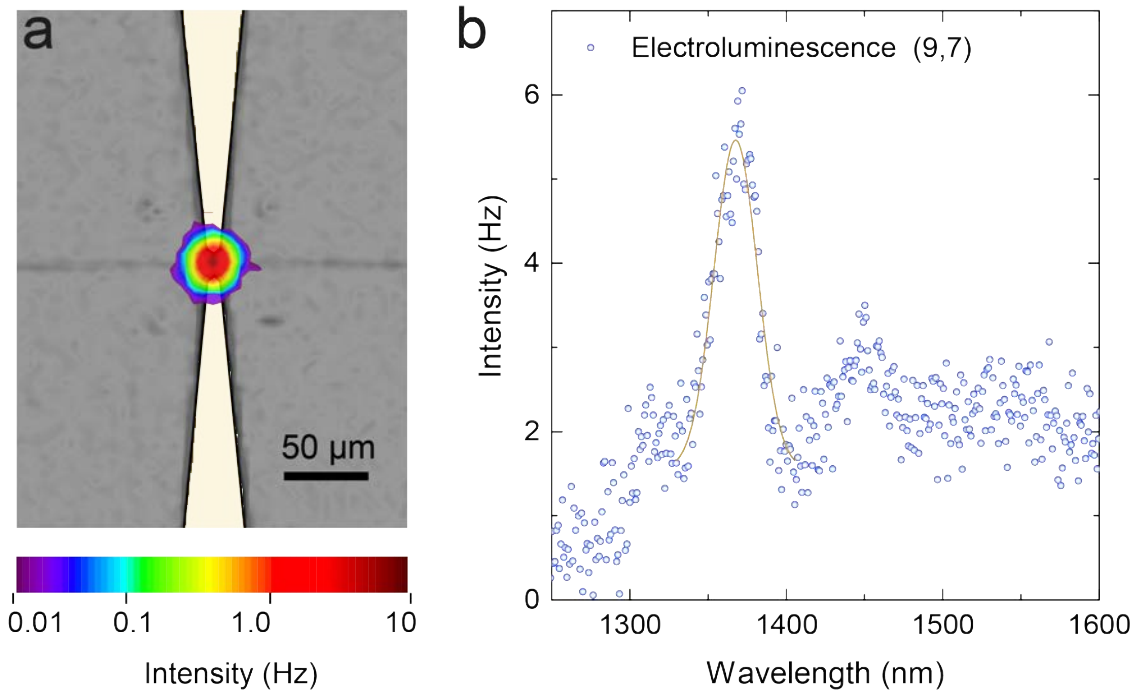
Non-classical light emission

Integrated quantum photonic circuit with CNT emitter



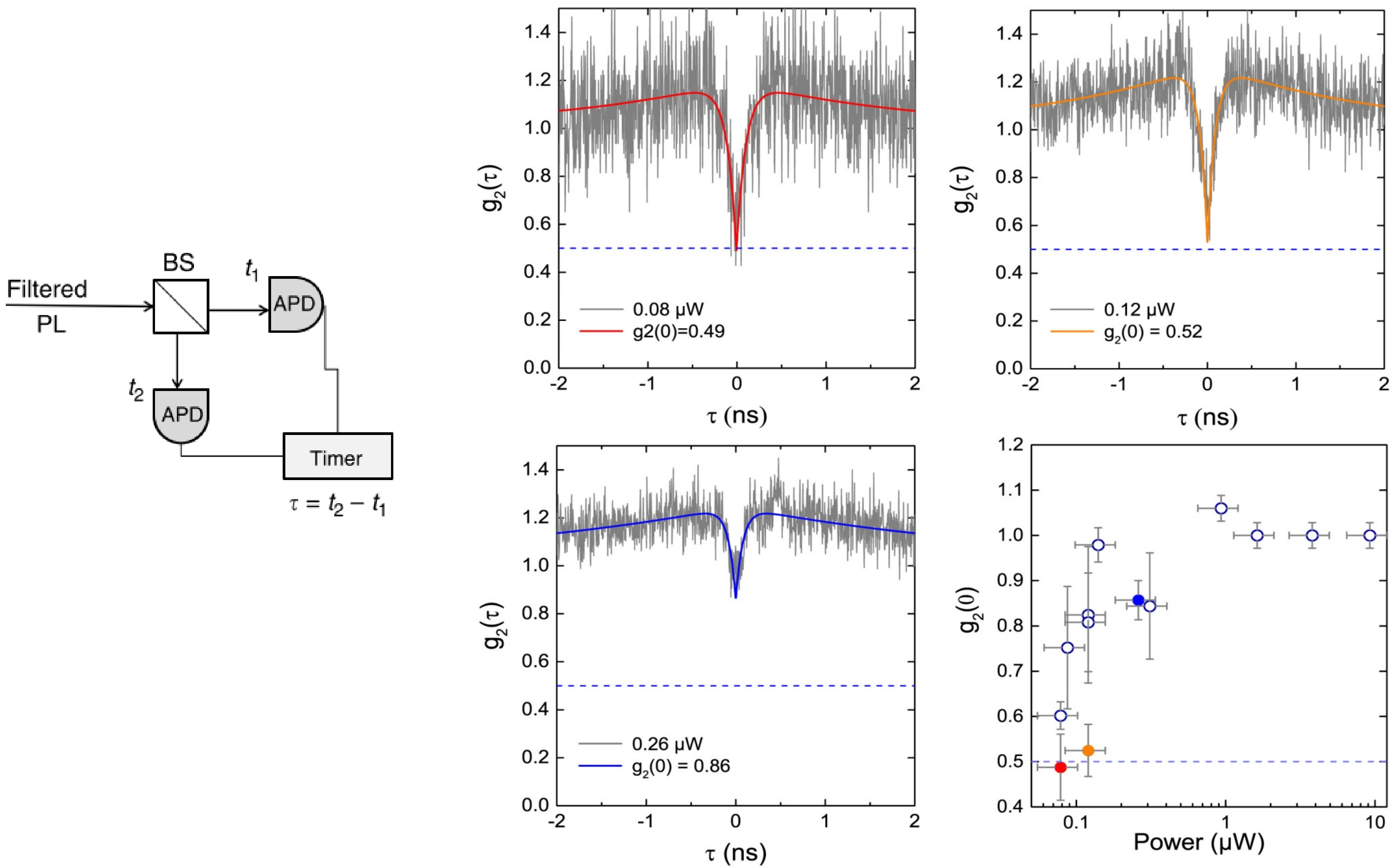
S. Khasminskaya, F. Pyatkov, S. Ferrari, O. Kahl, V. Kovalyuk, P. Rath, A. Vetter, K. Słowik, F. Hennrich, M. M. Kappes, G. Golt'sman, A. Korneev, C. Rockstuhl, RK, W. Pernice, Nature Photonics published 26.09.2016

Emission in NIR

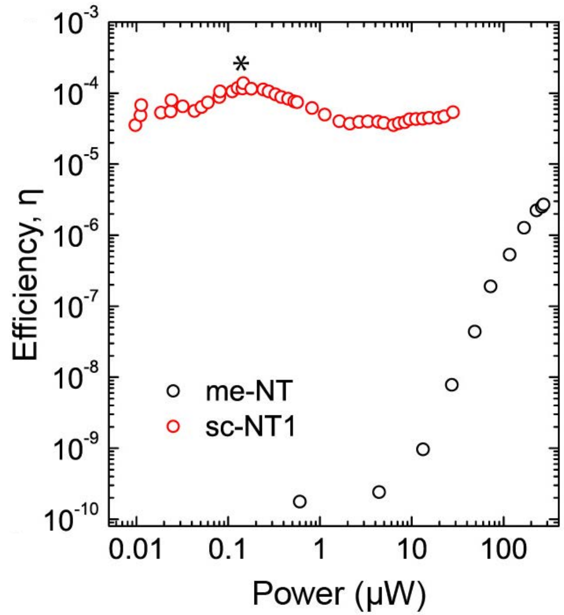


RT

Correlation experiments in Hanbury-Brown-Twiss configuration



Count rates, efficiency and mechanism

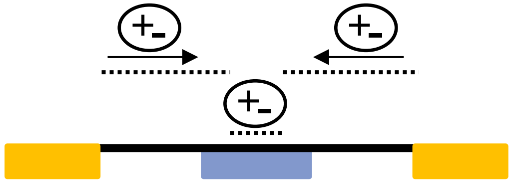


Low bias

count rate ∝ current · efficiency (T)

Low bias: count rate ∝ $T \cdot T^{1/2}$

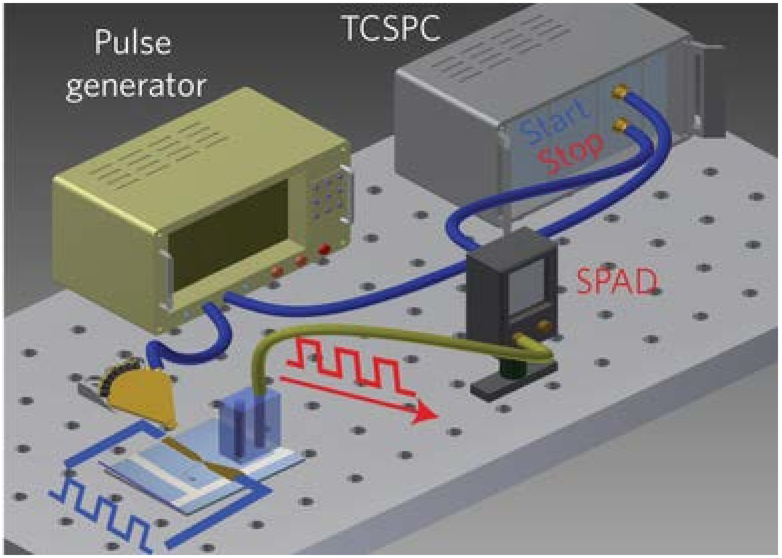
Medium bias: count rate ∝ $T \cdot T^{-1/2}$

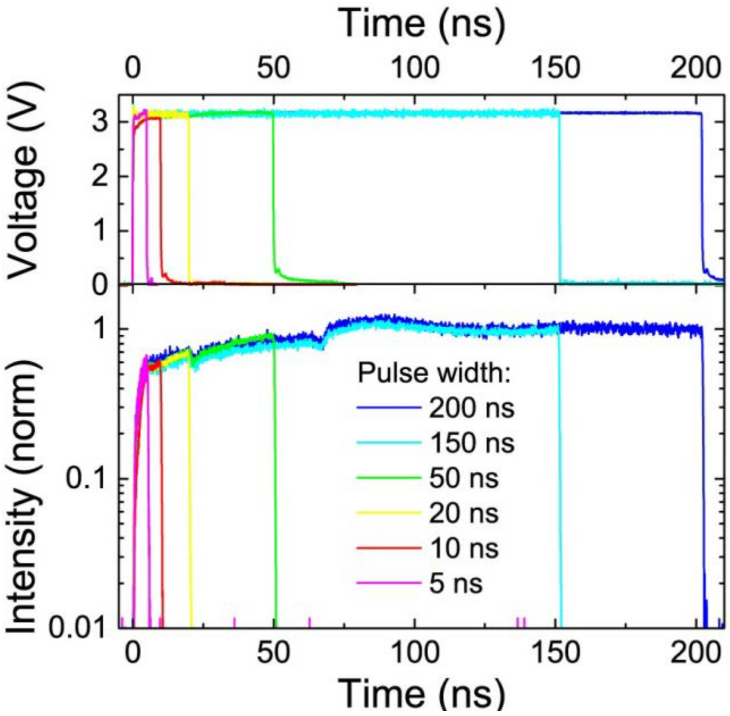


Diffusion length ∝ $T^{1/2}$

High-speed transducers

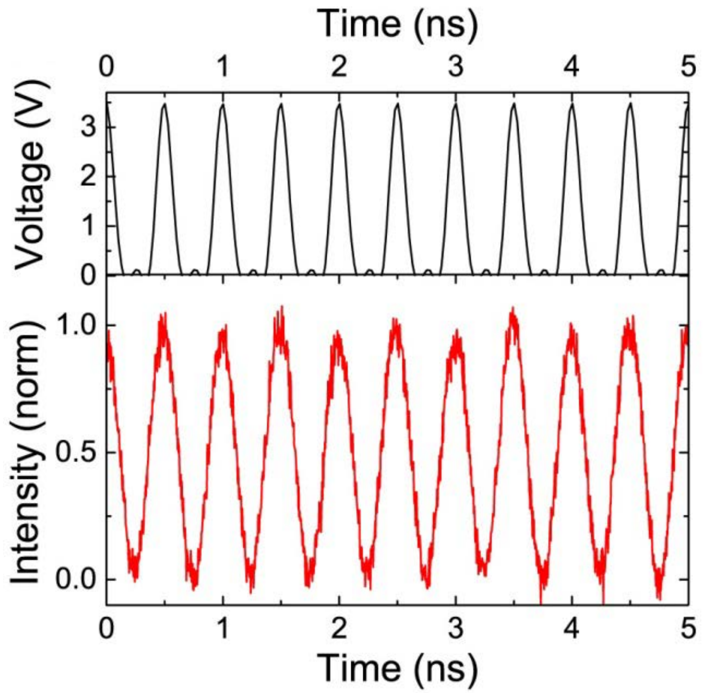
How fast is a WG-CNT-based electro-optical transducer ?

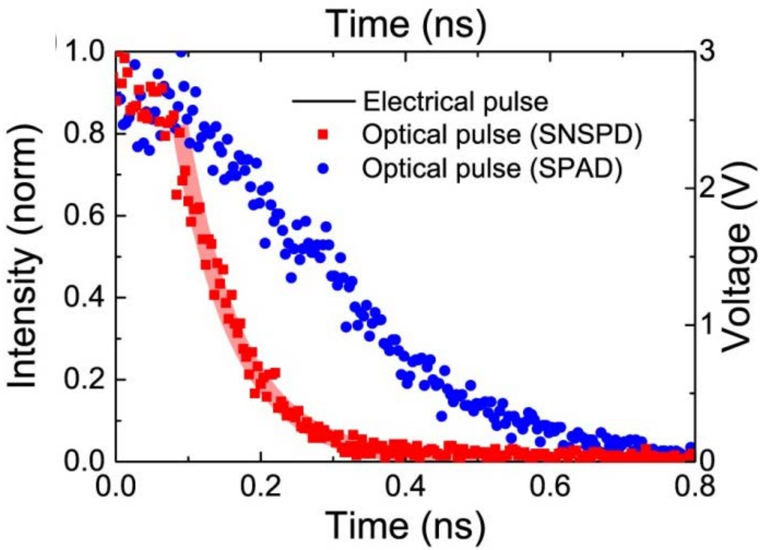




F. Pyatkov, S. Khasminskaya, V. Kovalyuk, F. Hennrich, M.M. Kappes, W.H.P. Pernice, RK, Beilstein J. Nanotechnol. 2017

How fast is a WG-CNT-based electro-optical transducer ?





→ Characteristic time scale < 80ps (>125GHz), limited by measurement setup.

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Karlsruher Institut für Technologie

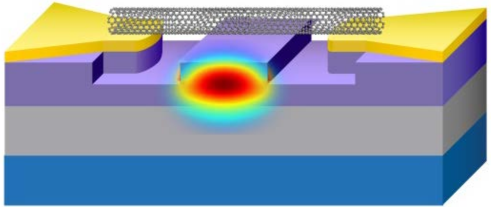
VolkswagenStiftung

DFG Deutsche Forschungsgemeinschaft

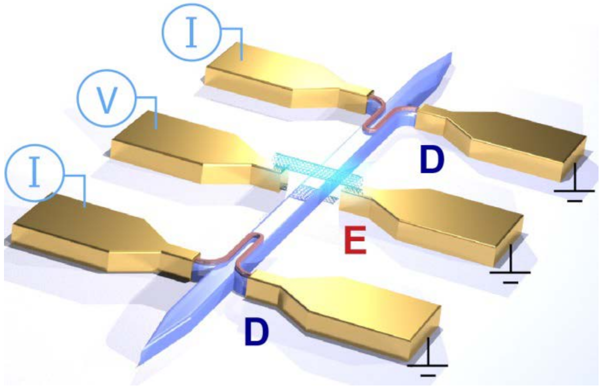
TECHNISCHE UNIVERSITÄT DARMSTADT

Summary

- Waveguide-integrated carbon nanotube emitter
  Advanced Materials 26 (**2014**) 3465; Optics Express 24 (**2016**) 966-974



- Tailoring emission linewidth and wavelength
  Nature Photonics 10 (**2016**) 420-427



- Non-classical light emission
  Nature Photonics 10 (**2016**) 727–732

- High frequency transducers
  Beilstein J. Nanotechnol. 8 **(2017)** 38–44

Review: Nature Materials 17 (2018) 663-670