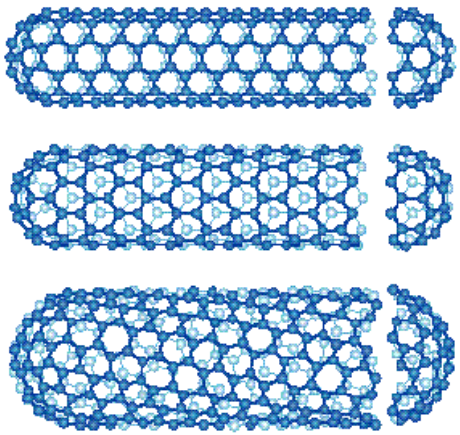
Functionalization of carbon nanotubes for the self-assembly of hybrid structures

Udo Beierlein

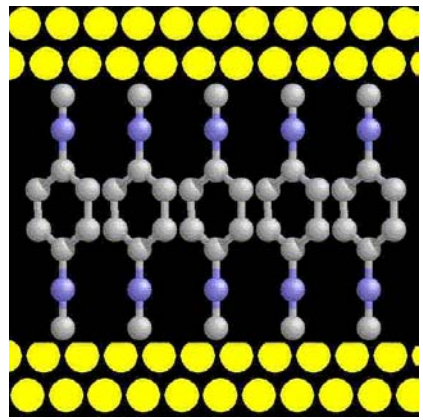
Department für Physik (LS Kotthaus)
and Center for NanoScience, LMU München

Molecular electronics group activities:

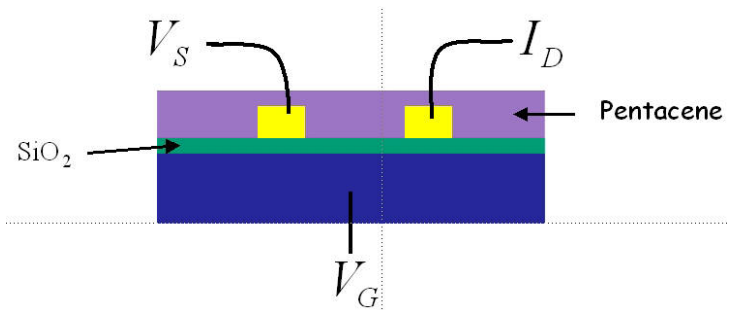
Carbon Nanotubes



Polyphenylene SAMs (= self-assembled monolayers)



Pentacene TFTs



Outline

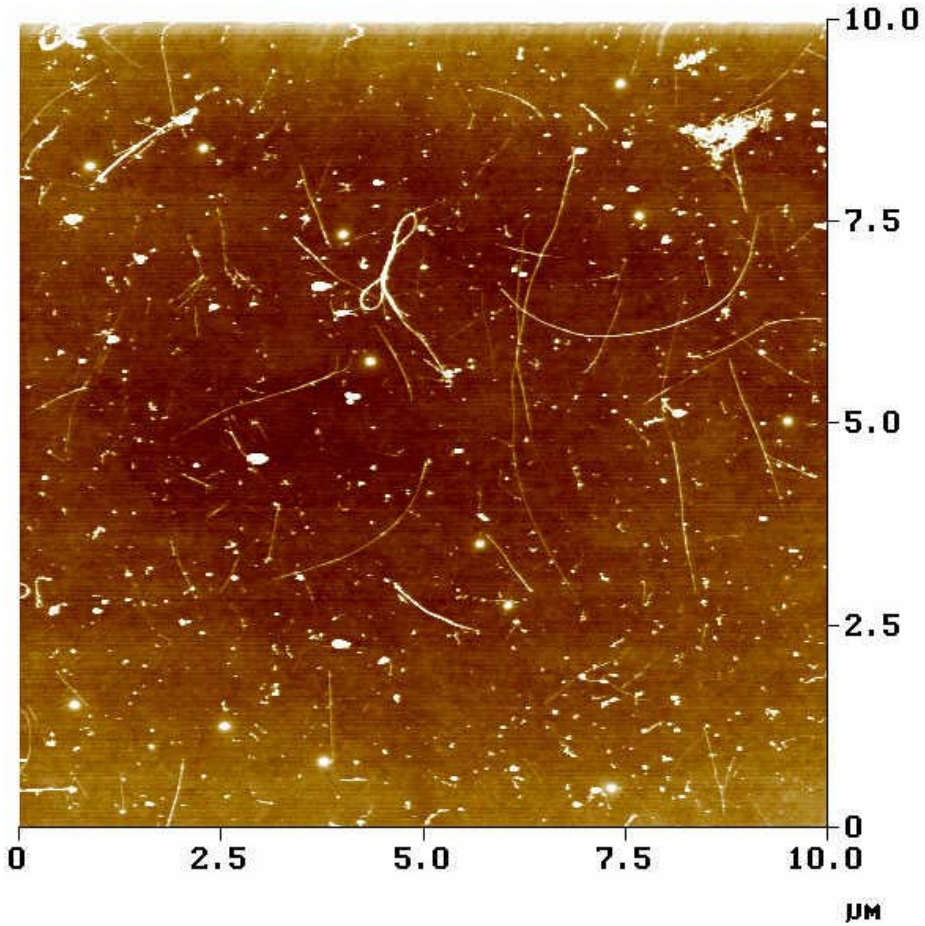
Non-covalent functionalization of CNTs

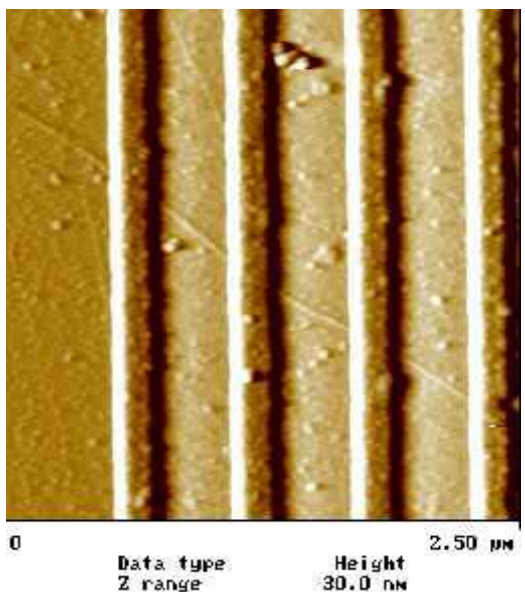
Covalent functionalization of CNTs

- chemical procedure
- attaching gold particles to CNTs by self-assembly
- electronic transport measurements
- catalytic gold enhancement
- thiolation of CNTs

Summary & Outlook

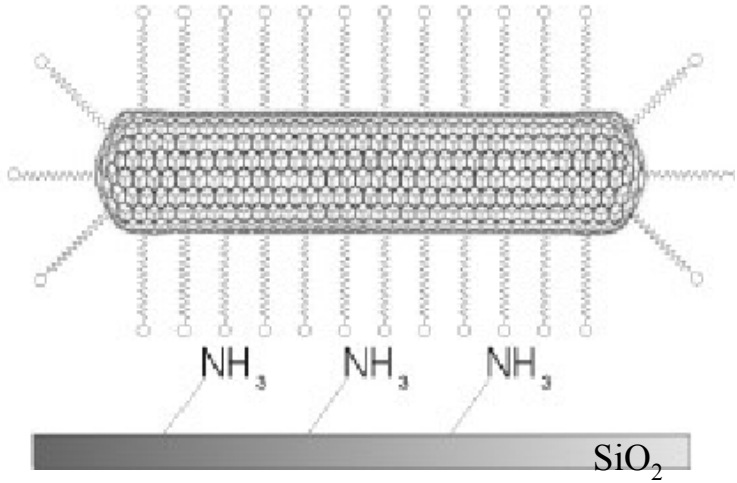
Motivation


10.0
7.5
5.0
2.5
0
0
2.5
5.0
7.5
10.0
µm


0
2.50 µm
Data type
Height
Z range
30.0 nm

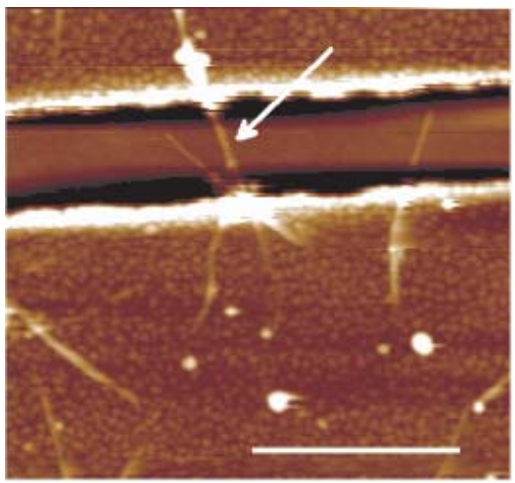
Non-covalent functionalization of CNTs

- Non-specific functionalization of carbon nanotubes with SDS:

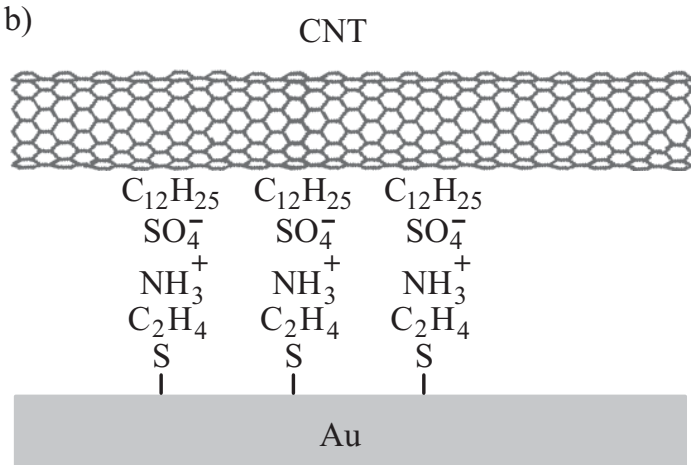


- Functionalization of gold electrodes with cysteamine:

a)

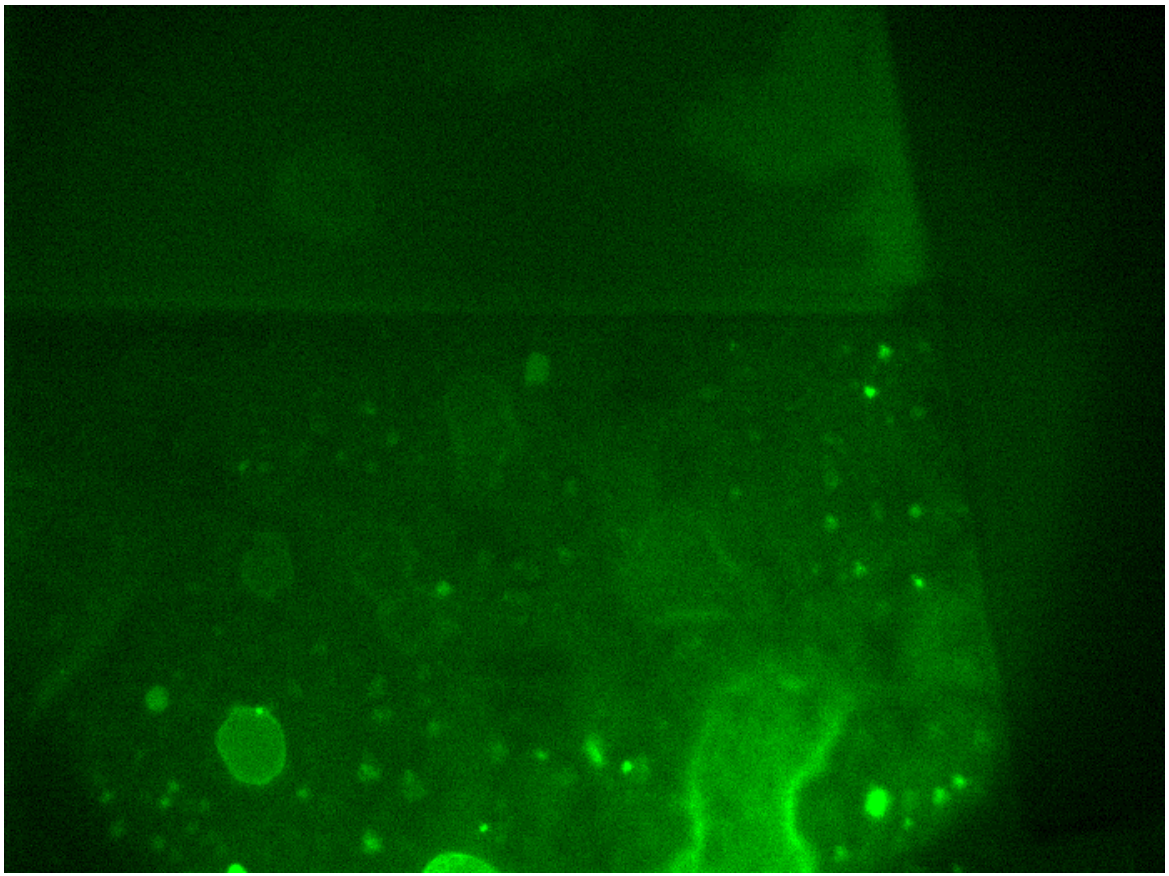


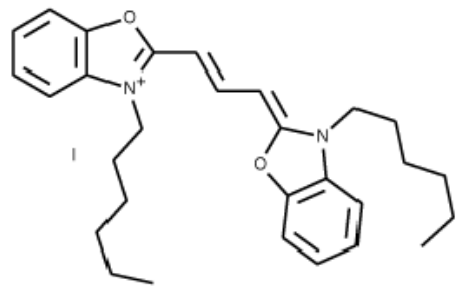
b)



AFM image of MWNTs bridging Au electrodes (scalebar: 1 μm)

Fluorescence labeling of MWNTs

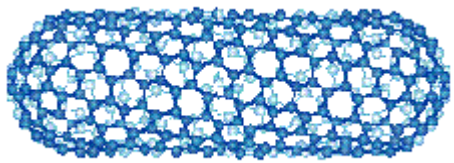


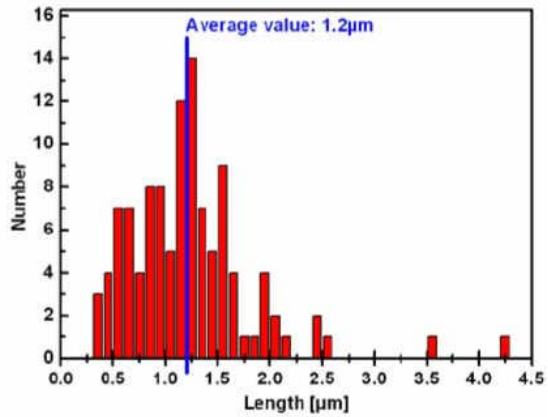


$DiOC_6$

Covalent functionalization: chemical procedure

1. step: acid treatment => carboxyl end-groups

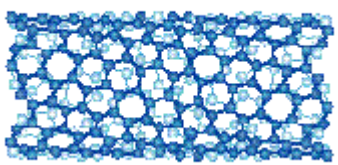


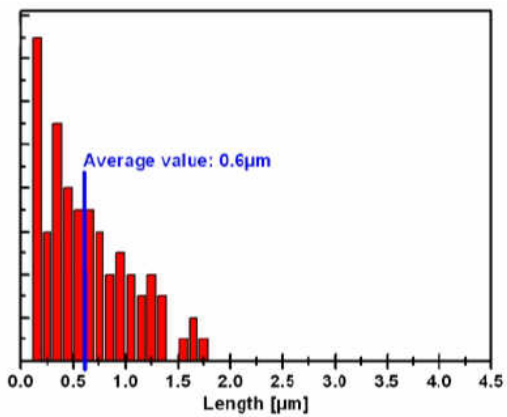


- nanotubes are usually endcapped
- length up to several microns

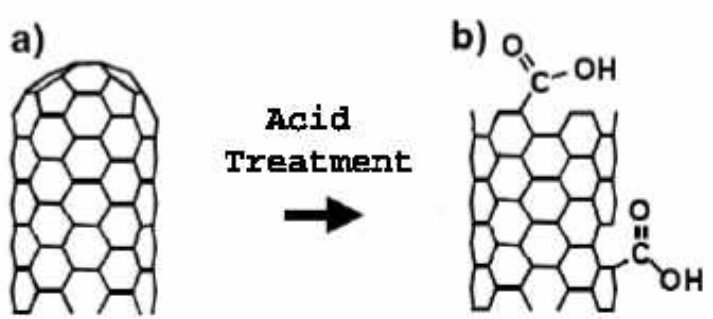
Ultrasonification in H_2SO_4/ H_2O_2 or in H_2SO_4/ HNO_3
+ filtration

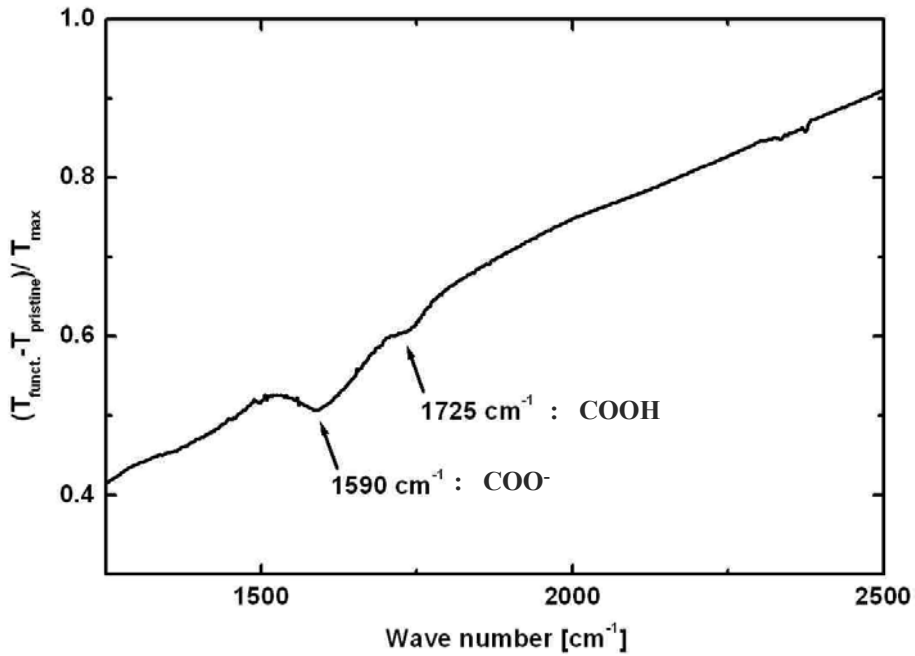
- nanotubes with open ends
- shortened in length
- „clean“ solution





Carboxyl end-groups as a starting point for chemical modifications





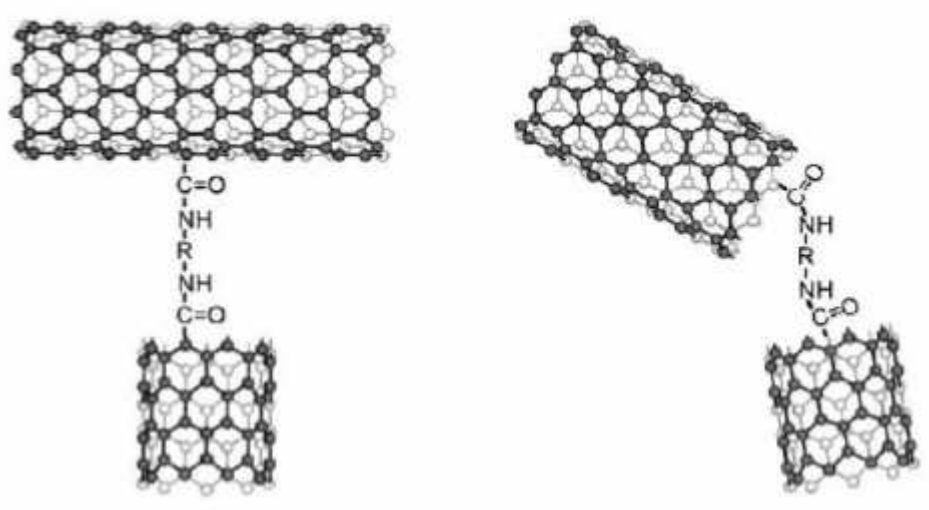
2. step: Conversion of the carboxyl groups to the corresponding acid chloride by refluxing in thionyl chloride

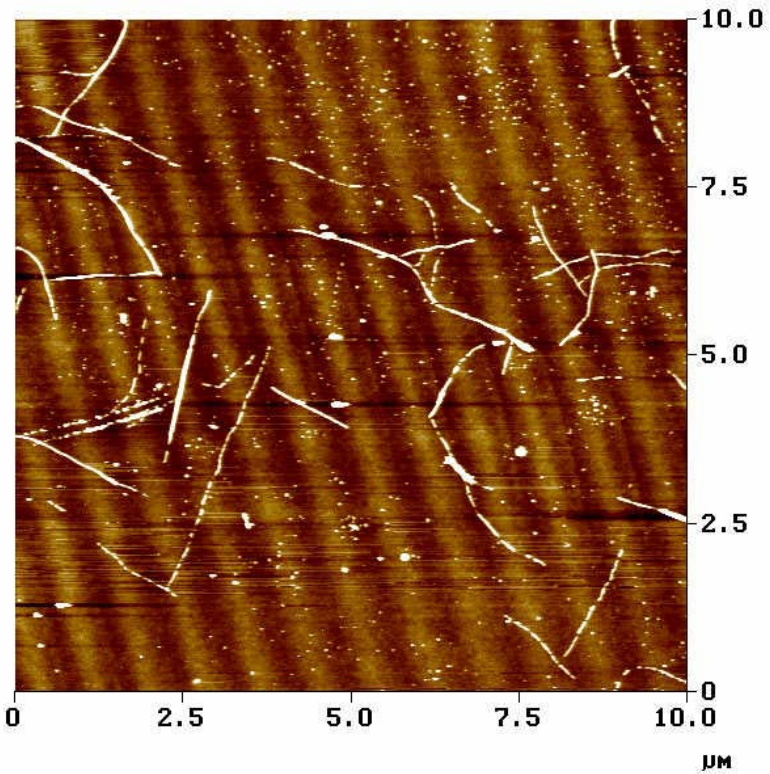
$$R\text{-}COOH + SOCl_2 \rightarrow R\text{-}COCl + SO_2 + HCl$$

The chlorine group is very reactive and allows versatile modification

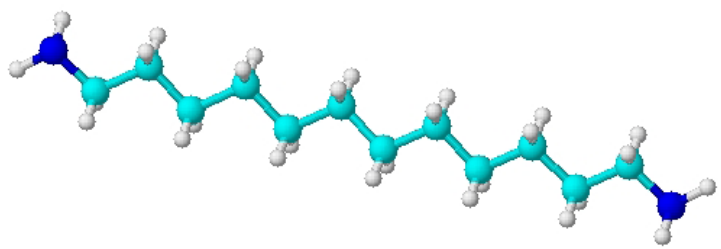
Test experiment: Attachment of molecular linkers

- Allows end-to-side as well as end-to-end interconnections





- linker: alkane chain



3. step: Biotinylation

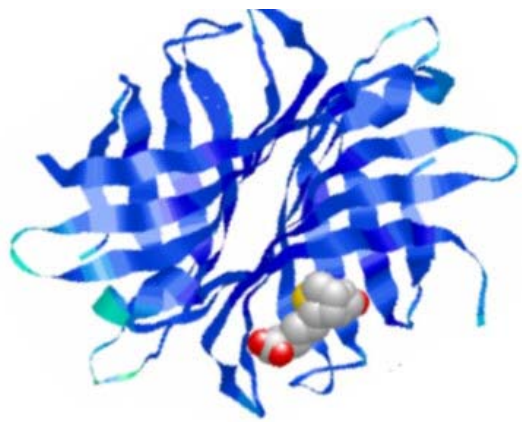
Sortiment...

biovit Biotin 5 mg - Intensivkur für Haut, Haare und Fingernägel

Schuppige Haut, brüchige Fingernägel und stumpfe Haare können Anzeichen für einen Biotin-Mangel sein.

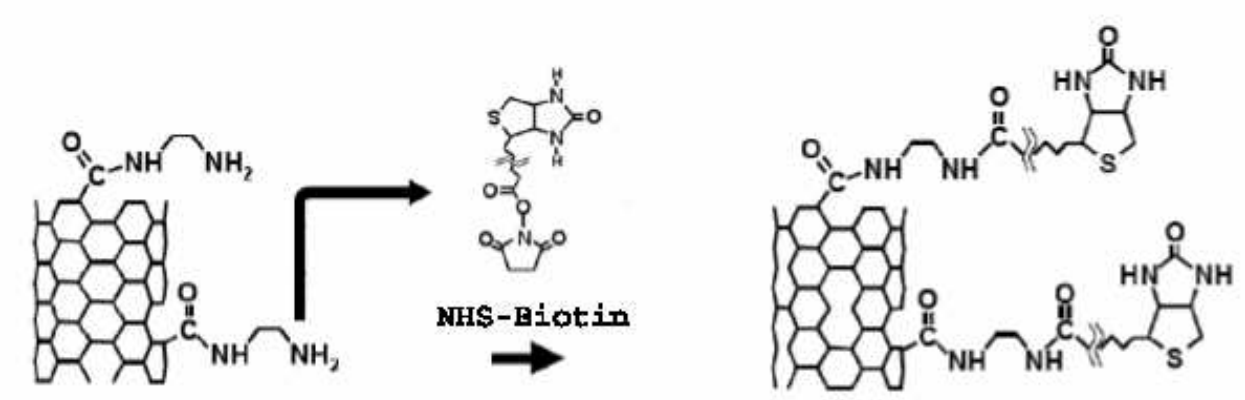
Biotin, auch Vitamin H (H für Haut) genannt, unterstützt den Stoffwechsel und trägt dazu bei, dass der Körper genügend Keratin bilden kann. Für Haut, Haare und Fingernägel ist Keratin eine wichtige Voraussetzung für ein gesundes Wachstum und die richtige Versorgung. Es verleiht ihnen Festigkeit und Widerstandskraft. Biotin wirkt somit auf die Keratinstrukturen im Sinne einer sichtbaren und spürbaren qualitativen Verbesserung.

- Biotin is a vitamine that binds specifically to its corresponding protein streptavidin
- The biotin-streptavidin interaction is the strongest non-covalent binding in nature
- Up to four biotin molecules can bind to one streptadvidin

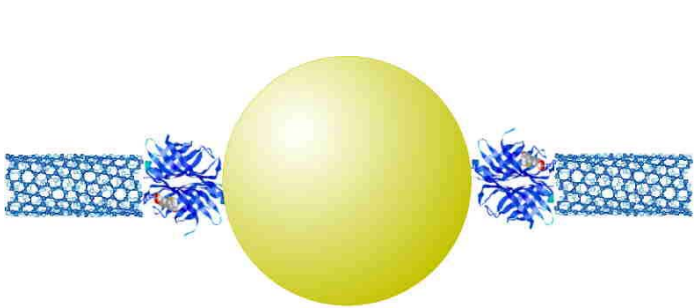


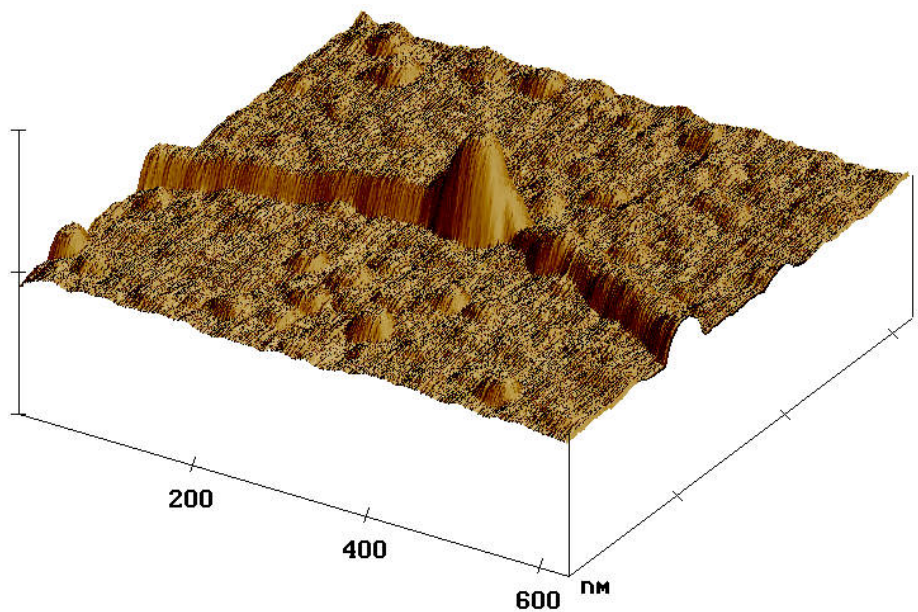
Biotinylation

- replace chloride by ethylenediamine
- attach NHS-biotin



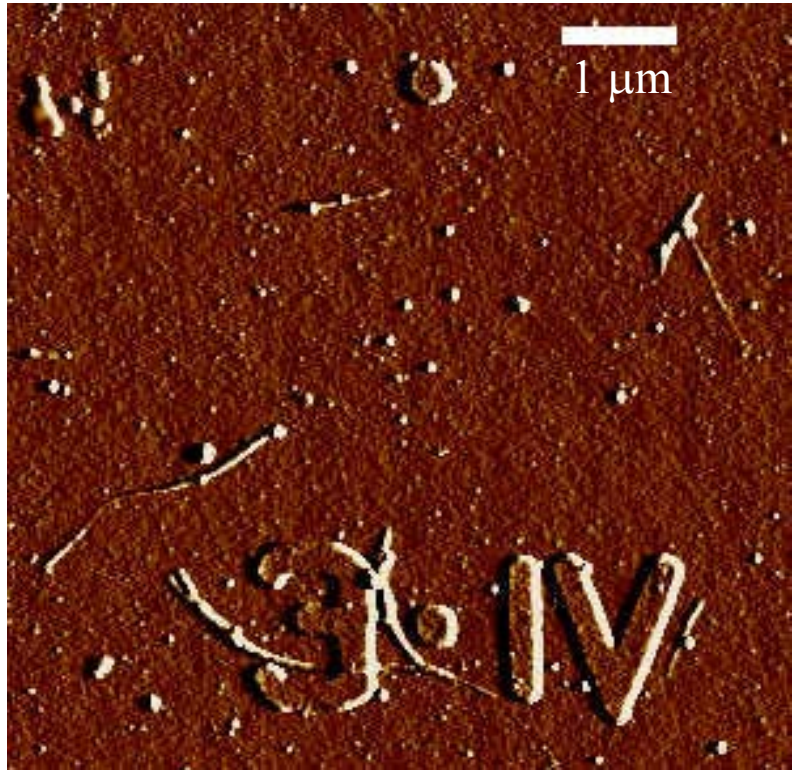
4. step: react with streptavidin-modified gold particles

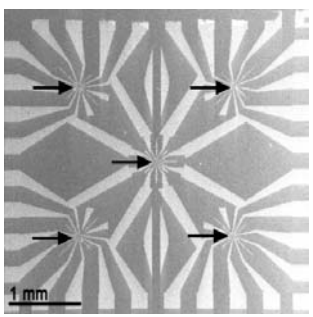




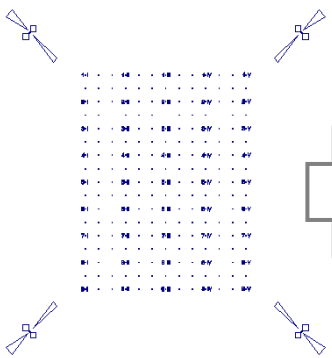
5. step: making contacts

• apply CNT-nanoparticle solution on a Si chip
• locate interesting structures with AFM
• make contacts using optical and e-beam lithography

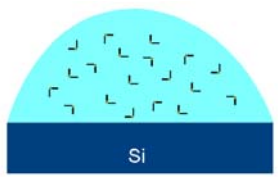




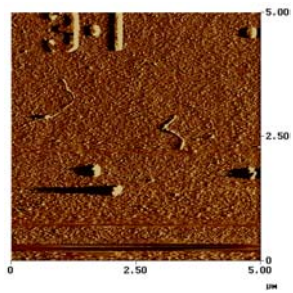
optically defined supply lines



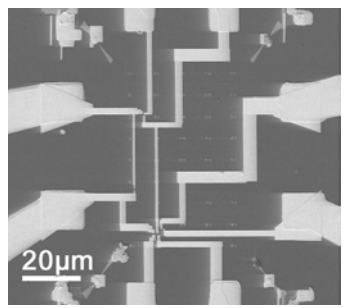
e-beam defined raster



deposition of droplet with functionalized tubes on the chip

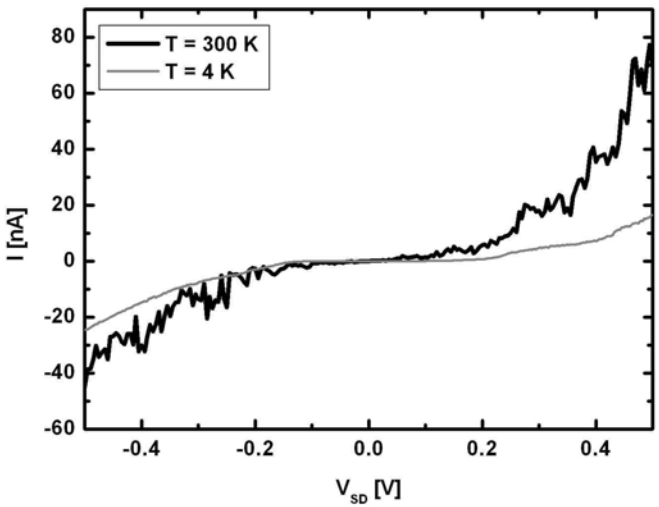


location of deposited tubes by AFM

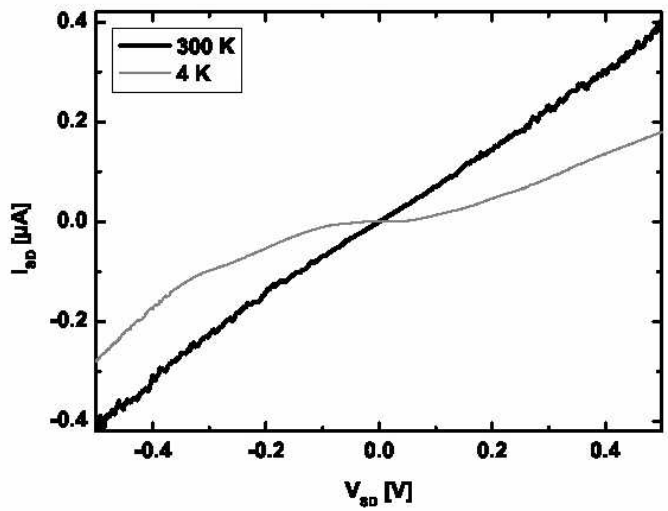


contacting of indi-vidual nanotubes

Electronic transport measurements

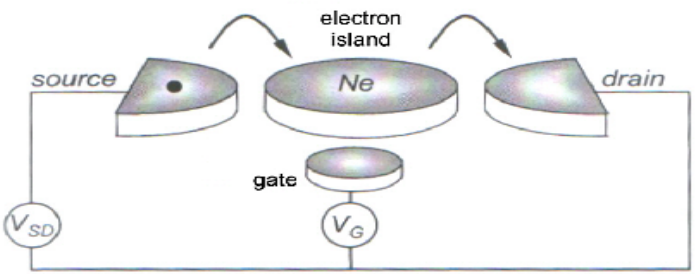


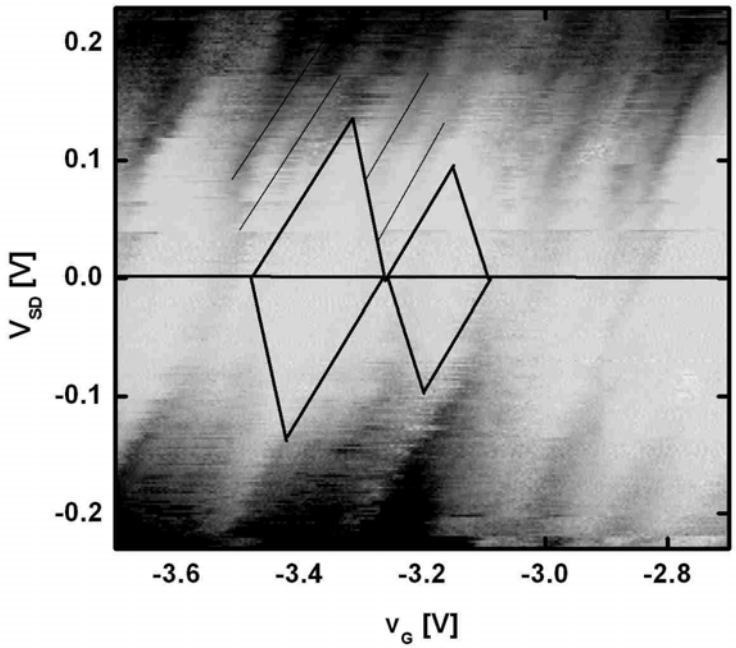
Non-linear source-drain curve at
$T = 300$ K and at $T = 4.2$ K:
At least one of the two SWNTs
is semiconducting



Linear source-drain curve at
$T = 300$ K and non-linear at $T = 4.2$ K:
two metallic SWNTs
Coulomb blockade at low T

Coulomb blockade





$$E_C = \frac{e^2}{C}$$

$$C_{CNT} = \frac{2\pi\varepsilon_r\varepsilon_0 L}{\ln(2z/r)}$$

$$C_{Colloid} = 4\pi\varepsilon_r\varepsilon_0 r$$

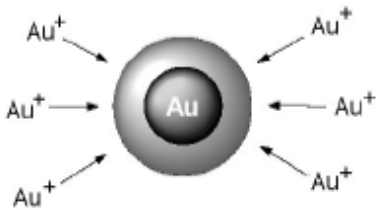
Charging energies:

$E_{C,small}$ ~ 93 meV C_{small} ~ 1.7 aF $L_{CNT,small}$ ~ 94 nm $r_{colloid,small}$ ~ 7.7 nm

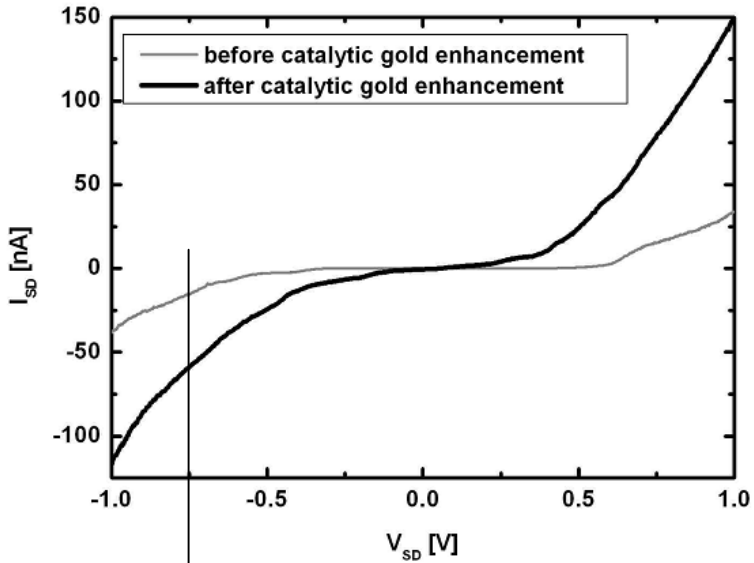
$E_{C,big}$ ~ 135 meV C_{big} ~ 1.2 aF $L_{CNT,big}$ ~ 65 nm $r_{colloid,big}$ ~ 5.3 nm

Catalytic gold enhancement

The contacted colloids with d = 25 nm have been enlarged by catalytic gold enhancement

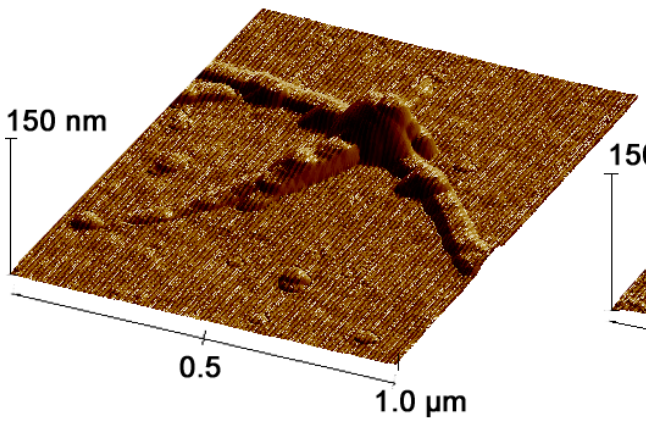


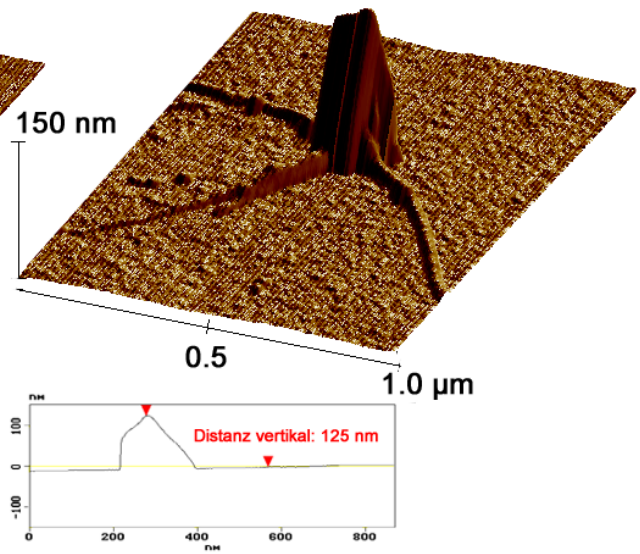
Au-ions are refined at the seed metal in the presence of a reducing agent



Factors, the resistance was decreasing at V = -0.75 V:

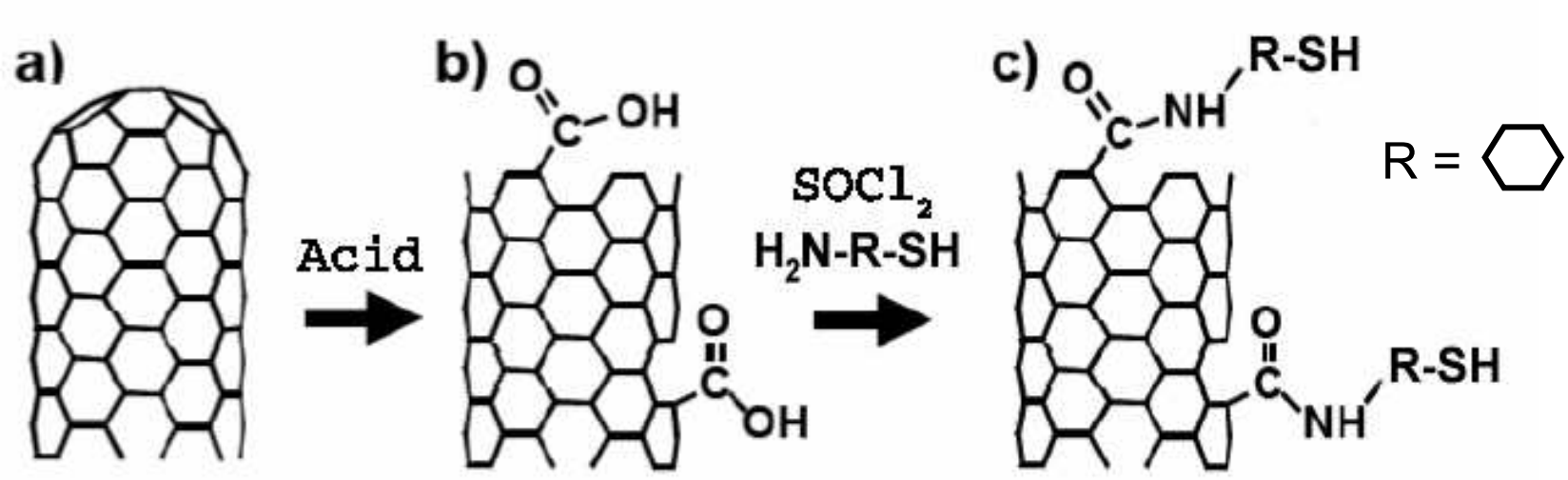
	factor
5 Samples	2 - 9
2 Samples	0
1 Sample	short circuit





Two AFM-pictures of a colloid with d = 25 nm, before and after 2 minutes incubation with Nanoprobe Goldenhance

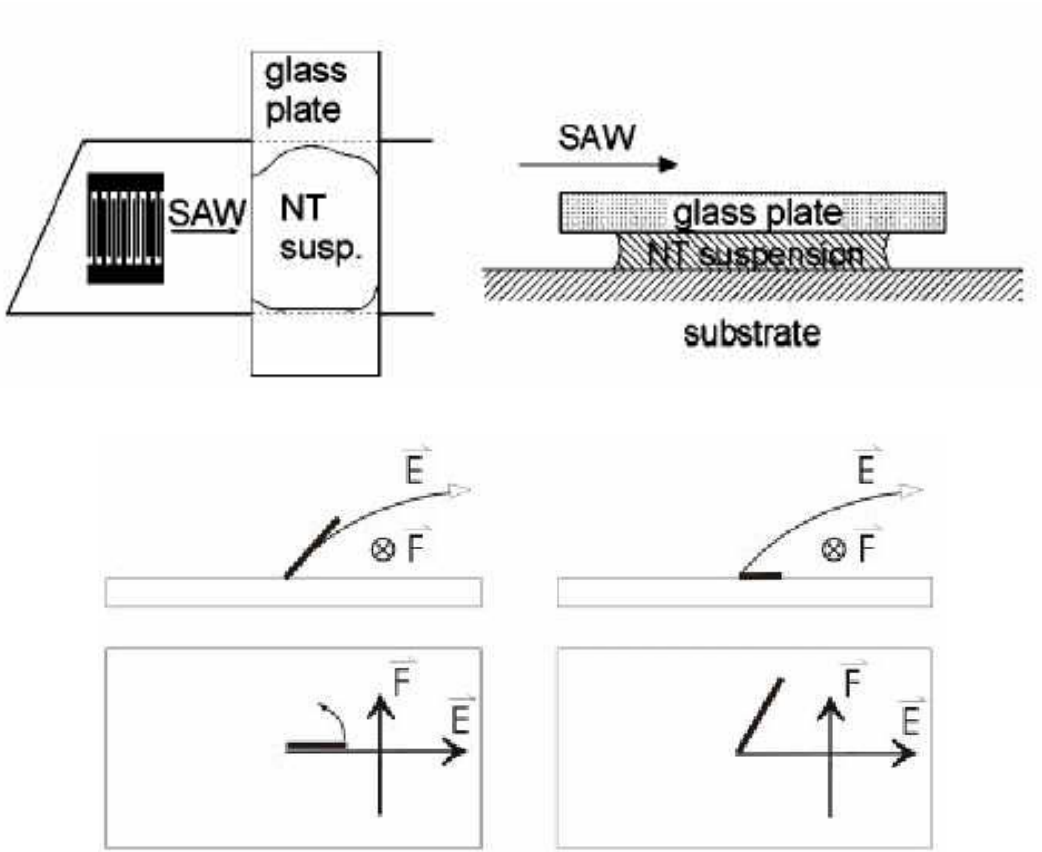
Thiolation of CNTs

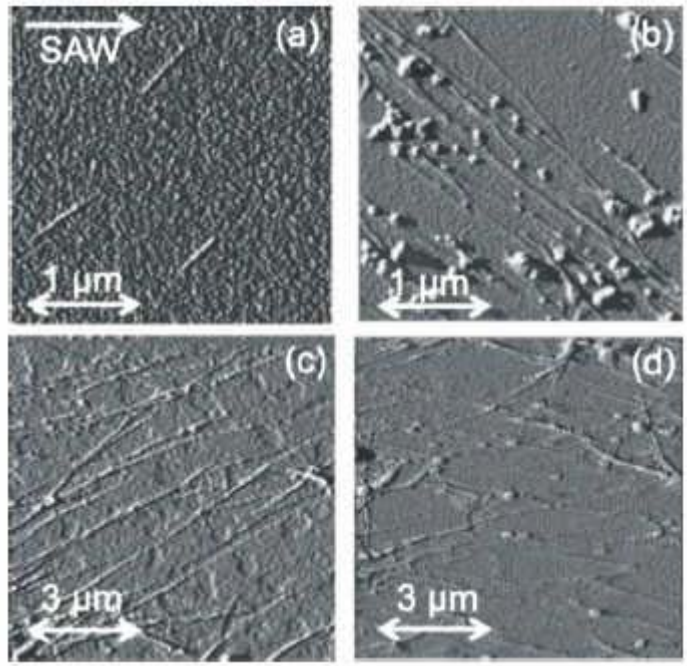


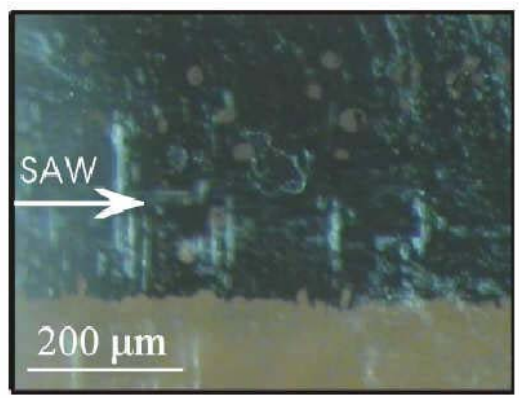
Self-assembly of CNTs on contacts?

CNT alignment by surface acoustic waves

in collaboration with C. Strobl, J. Ebbecke, A. Wixforth, Uni Augsburg

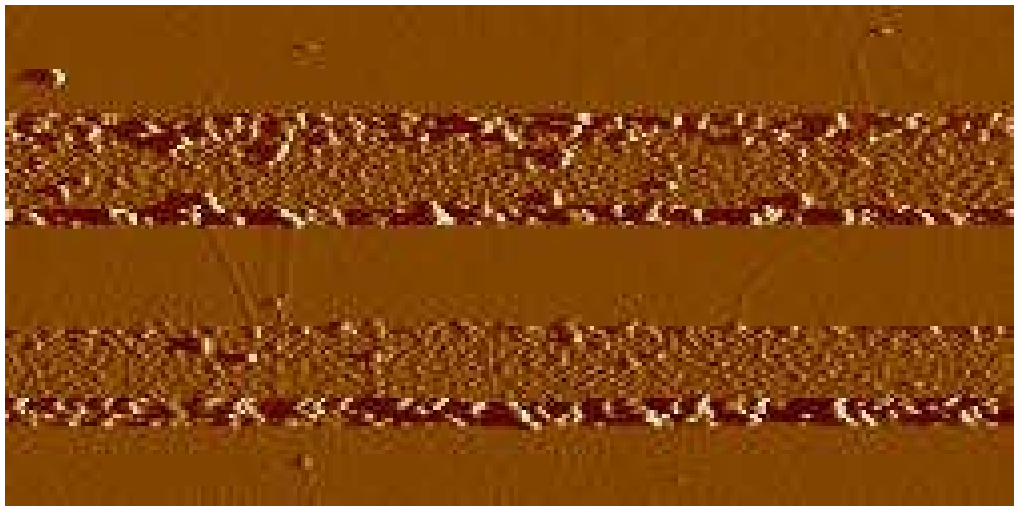


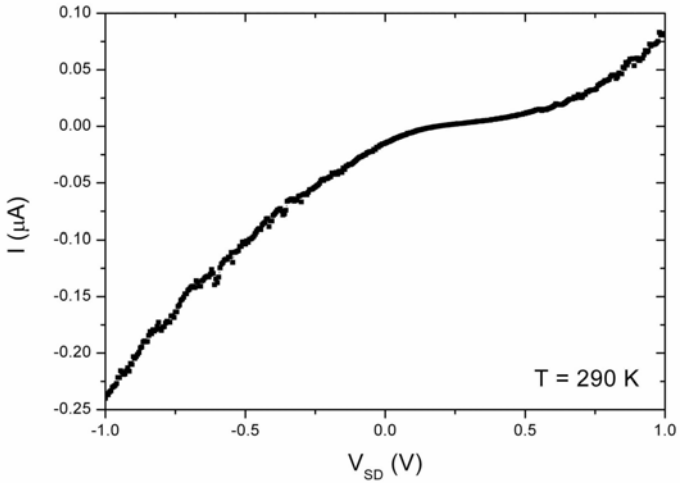


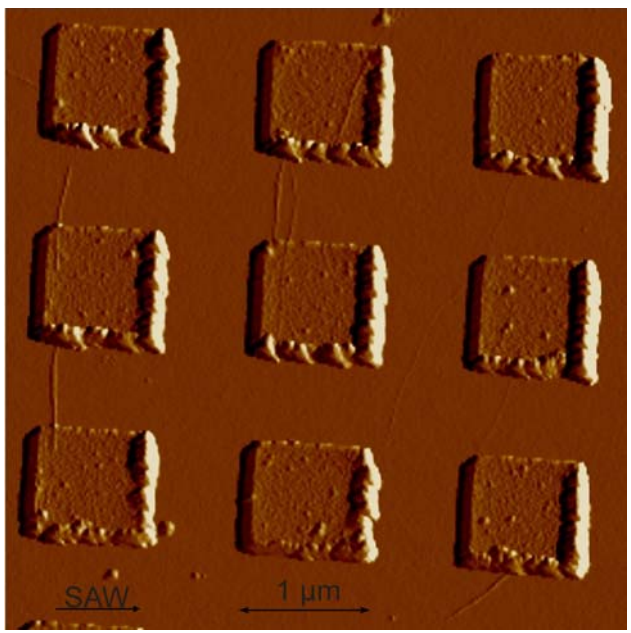


C. Strobl, C. Schäflein, U. Beierlein, J. Ebbecke, A. Wixforth, APL 85, 1427, 2004

Thiolated CNTs on gold contacts







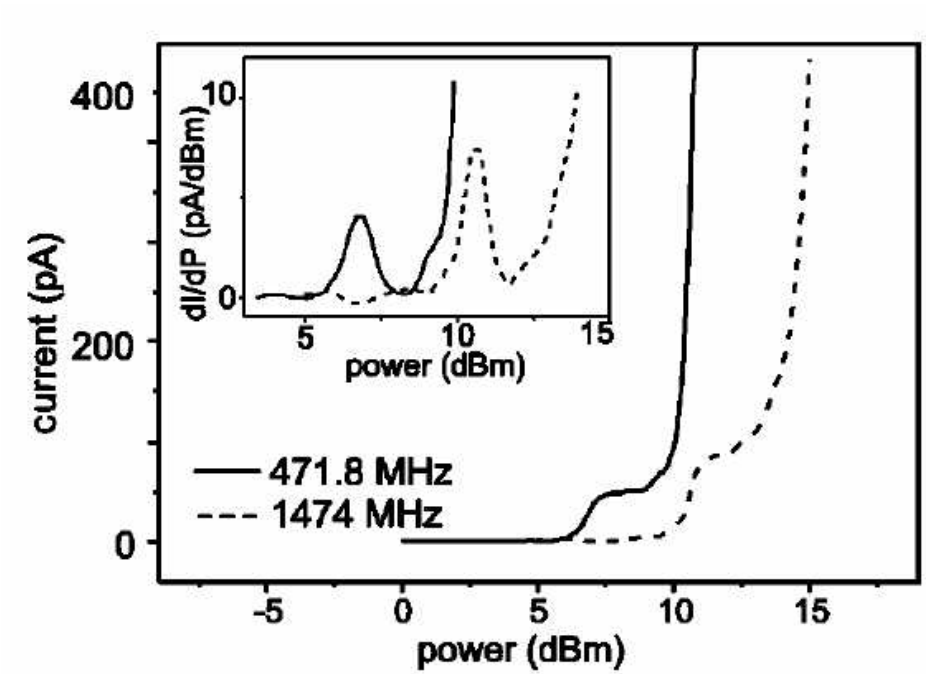
PHYSICAL REVIEW B **70**, 233401 (2004)

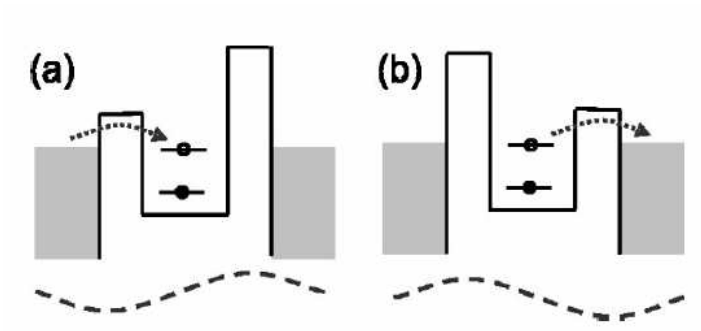
Acoustoelectric current transport through single-walled carbon nanotubes

J. Ebbecke,[1,*] C. J. Strobl,[2] and A. Wixforth[1]

[1]*Institut für Physik der Universität Augsburg, Experimentalphysik I, Universitätsstrasse 1, 86135 Augsburg, Germany*

[2]*Sektion Physik der Ludwig-Maximilians-Universität and Center for NanoScience (CeNS), Geschwister-Scholl-Platz 1, 80539 Munich, Germany*





Summary

- CNTs can be chemically modified in order to achieve some degree of molecular recognition and self-assembly

- SWNTs were connected via gold colloids

- These systems were individually electrically contacted and characterized in their electronic properties

- SWNTs were attached to electrodes via thiol-groups using SAW

Thanks

Christian J.-F. Dupraz

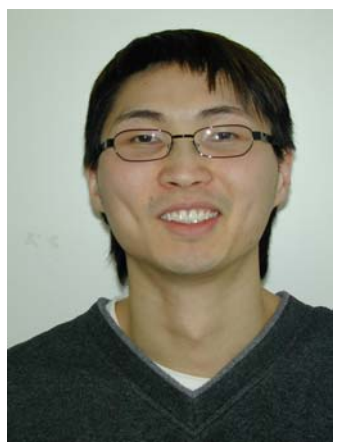
Tobias Smorodin

Carla Abilio

Prof. Jörg P. Kotthaus

LMU

CeNS
Center for NanoScience
Ludwig-Maximilians-Universität



Nok Tsao

Matthias Fiebig