Kohlenstoff-basierte Nanomaterialien: Aus der Forschung in die Anwendung

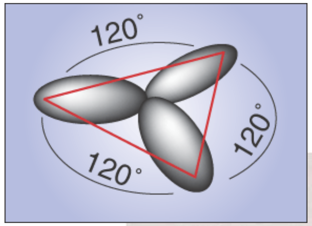
Oliver Gröning
Eidg. Materialprüfungs- und Forschungsanstalt
nanotech@surfaces Laboratory
8600 Dübendorf

Trends in Micro Nano
Brugg 23ter April 2015

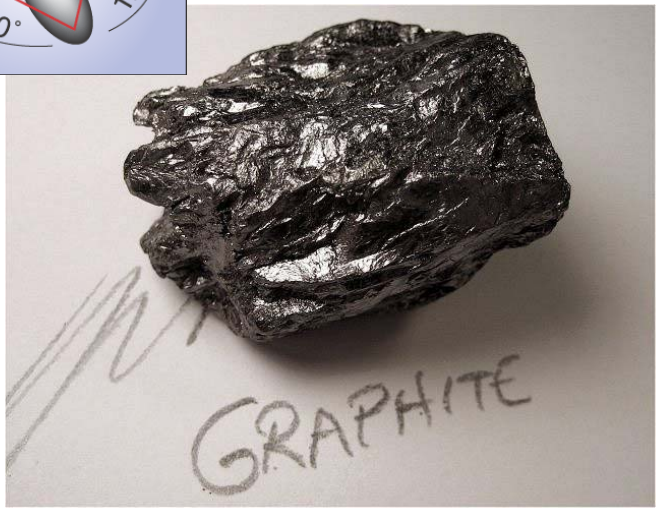
Die natürlichen Erscheinungs-formen des reinen Kohlenstoffs

6 12.011
±4,2
4470
4100
C
2.62
$1s^2 2s^2 p^2$
Carbon

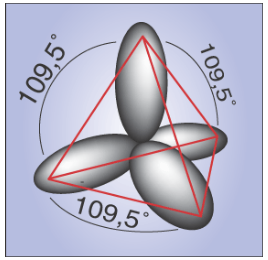
EMPA
Materials Science & Technology



sp^2 Kohlenstoff



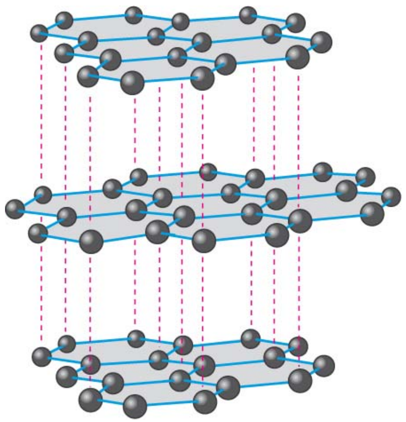
sp^3 Kohlenstoff

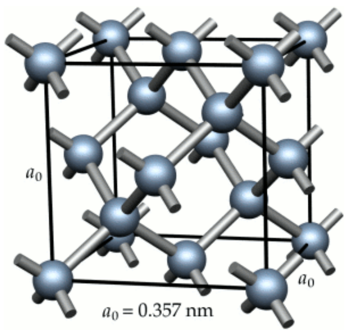


Graphit:

2-dimensional vernetzte Bindungsstruktur in einer Einzellage und Stapelung der Lagen mit schwachen Bindungskräften. Hochgradig anisotrop

3 kovalente Bindungen pro Atom





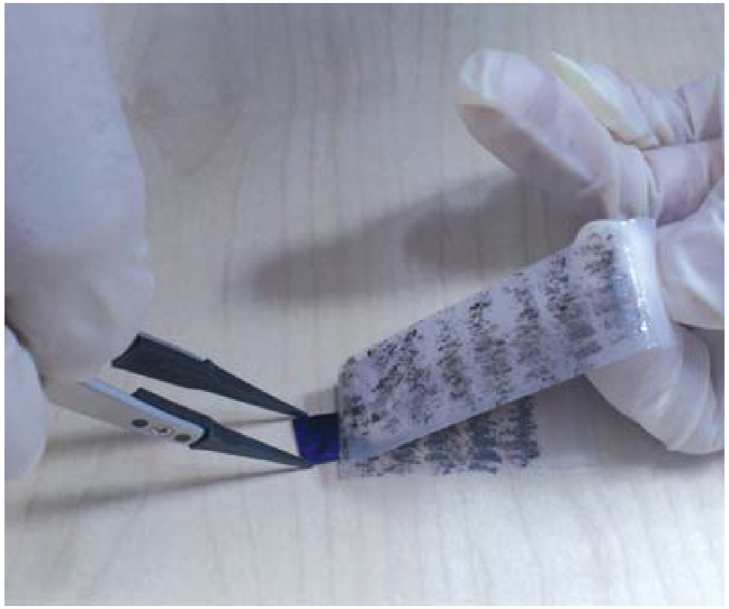
Diamant:

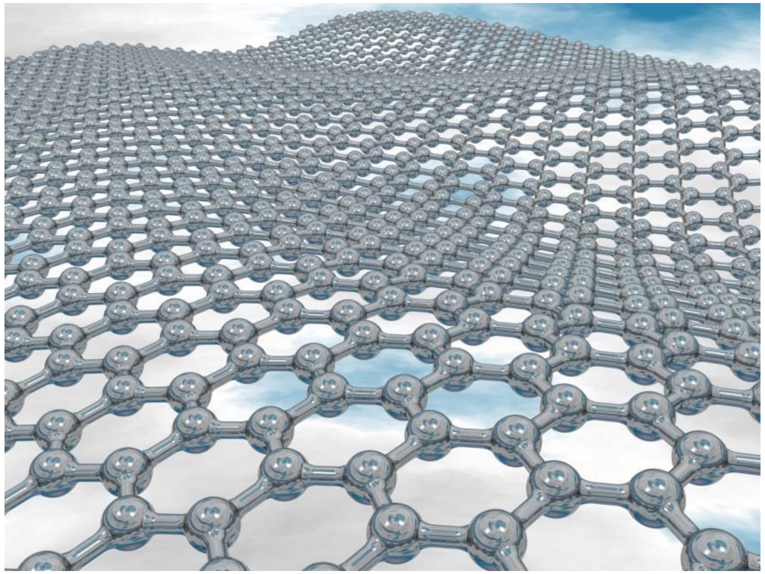
3-dimensional vernetzte Bindungsstruktur mit isotropen Eigenschaften

4 Kovalente Bindungen pro Kohlenstoffatom

Graphen: Eine einzelne Lage graphitischen Kohlenstoffs

6 12.011
±4,2
4470
4100
C
2.62
$1s^2 2s^2 p^2$
Carbon

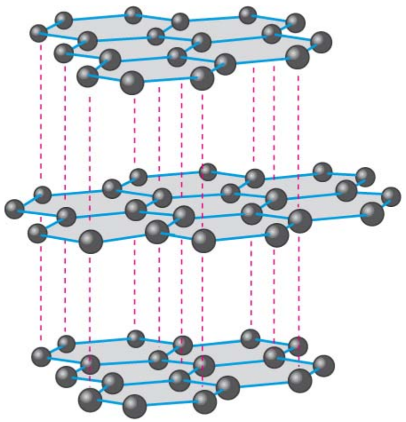




Graphit:

2-dimensional vernetzte Bindungsstruktur in einer Einzellage und Stapelung der Lagen mit schwachen Bindungskräften. Hochgradig anisotrop

3 kovalente Bindungen pro Atom

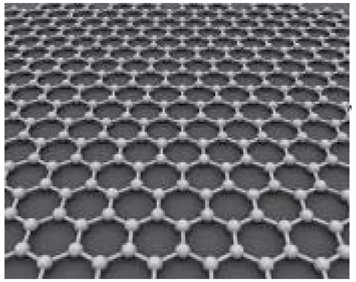


Graphene:

Einzelne Lage (d.h. ein Atom dick) graphitisch gebunden Kohlenstoffs

Erstmals isoliert in 2004 durch Geim und Novoselov

Die Superlativen des Graphen

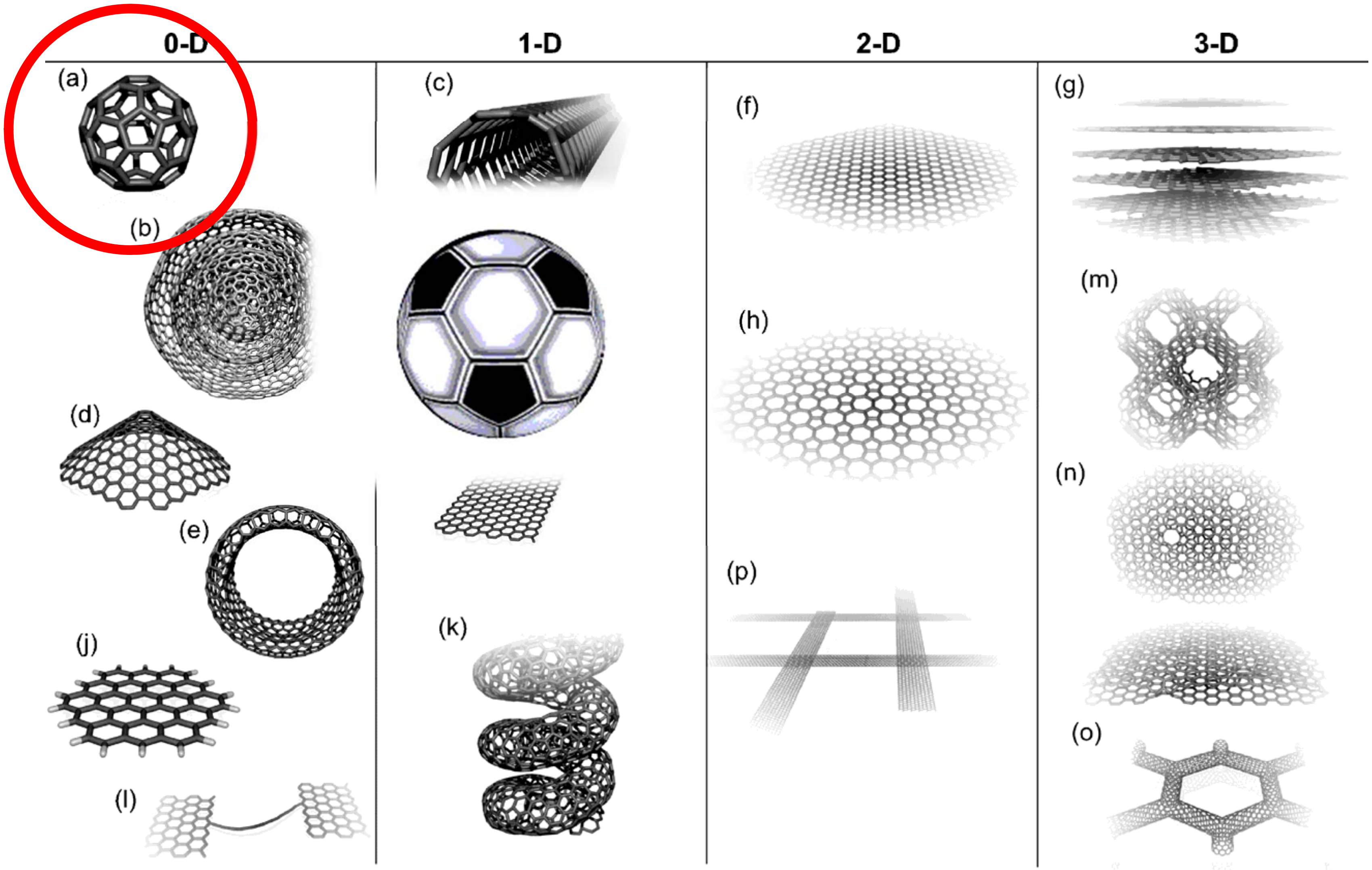


- *Das härteste bekannte Material*
- *Dünnstmögliche Membran*
- *Trotzdem undurchlässig für Gase*
- *Höchste thermische Leitfähigkeit bei Raumtemperatur*
- *Ballistischer Elektronentransport bei Raumtemperatur über Mikrometerdistanzen*
- *Kann Grössenordnungen höhere Stromdichten transportieren als Kupfer*
- *Quantenhalleffekt bei Raumtemperatur*
- *...*

	Graphen	**«Rivale»**
Elastizitätsmodul	1060 GPa	500 (WC)
Reissspannung	130 GPa	3.6 (Kevlar)
Elektronenmobilität	200’000 $cm^2V^{-1}sec^{-1}$	1’000 (Si), 8’500 (GaAs)
Elektrischer Widerstand	$1x10^{-8}$ Ωcm	1.6×10^{-8} (Ag)
Thermische Leitfähigk.	5000 $Wm^{-1}K^{-1}$	400 (Cu), 2000 (Diamant)
Spezifische Oberfläche	2630 m^2g^{-1}	
Permeabilität	Undurchlässig für He	

Übersicht graphitischer Nanostrukturen

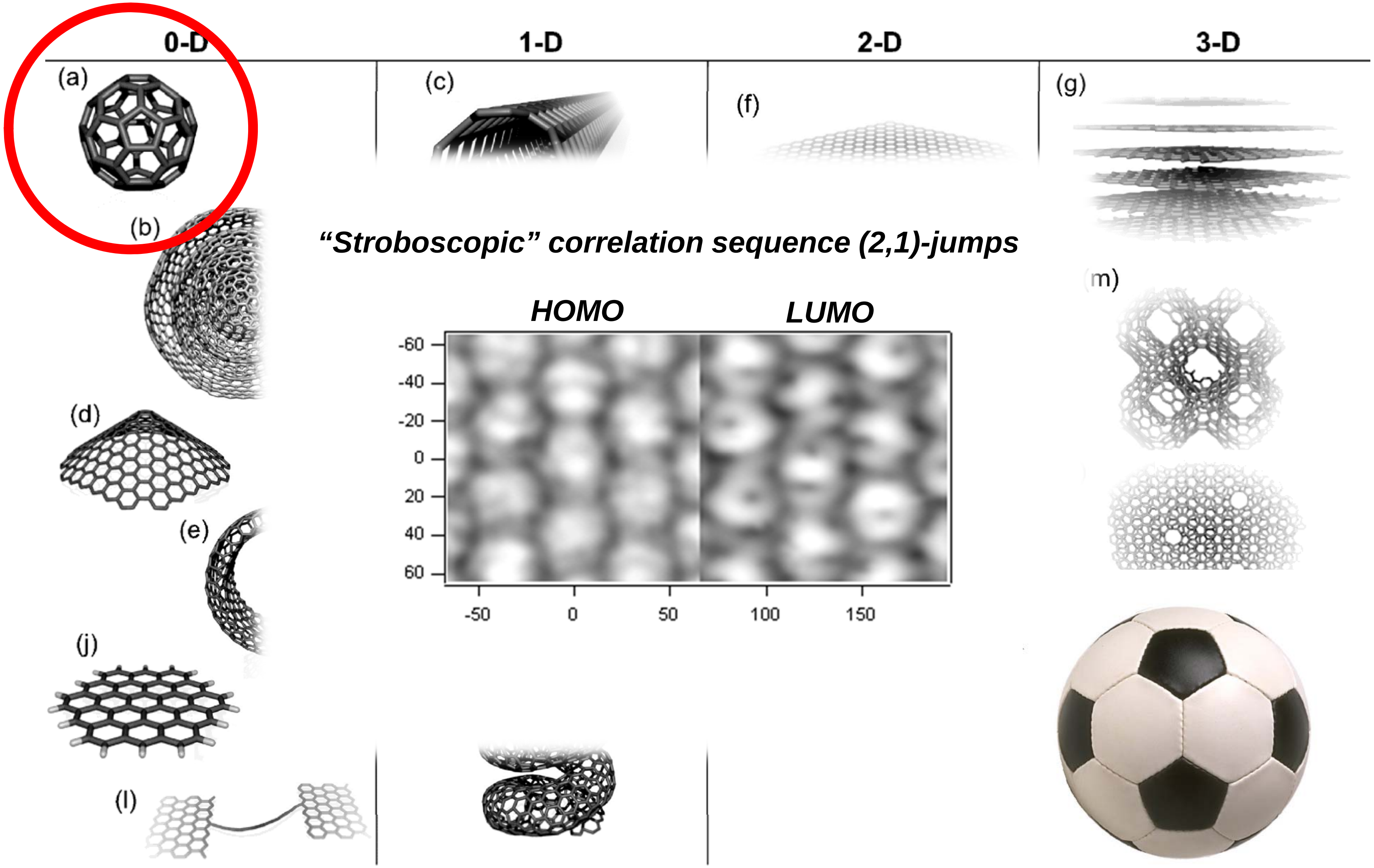
EMPA
Materials Science & Technology



M. Terrones et al., Nano Today (2010), doi:10.1016/j.nantod.2010.06.010

Übersicht graphitischer Nanostrukturen

EMPA
Materials Science & Technology



M. Terrones et al., Nano Today (2010), doi:10.1016/j.nantod.2010.06.010

Fullerene: C_{60} und darüber hinaus

EMPA
Materials Science & Technology

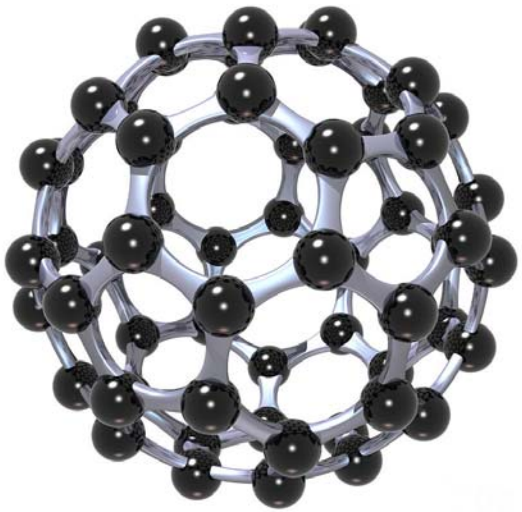
162 LETTERS TO NATURE NATURE VOL. 318 14 NOVEMBER 1985

C_{60}: Buckminsterfullerene

H. W. Kroto*, J. R. Heath, S. C. O'Brien, R. F. Curl & R. E. Smalley

Rice Quantum Institute and Departments of Chemistry and Electrical Engineering, Rice University, Houston, Texas 77251, USA

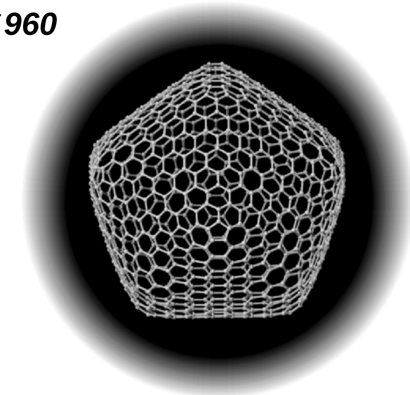
Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C_{60} molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.



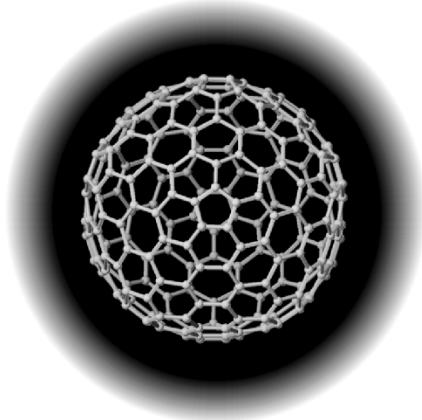
C_{60}

© R. Knightly fine arts America

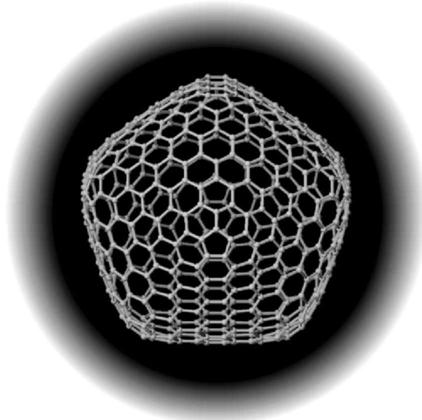
C_{960}



C_{240}



C_{510}

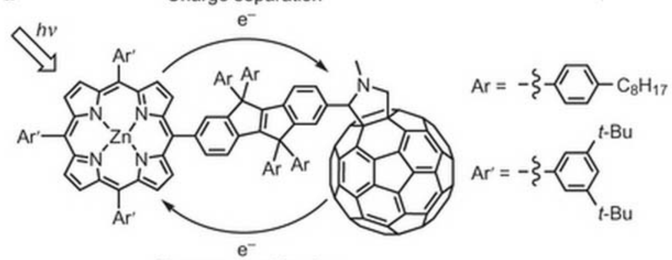


Adapted from: https://www.ccs.uky.edu/~madhu/Giant_Fullerene.html

Anwendungen:

- ***Organic electronics (PV, PD, OLED TFT) (e-Acceptor, n-type channel)***
- ***Photoresists for high resol. DUV***
- ***Antioxidant e.g. in cosmetics***

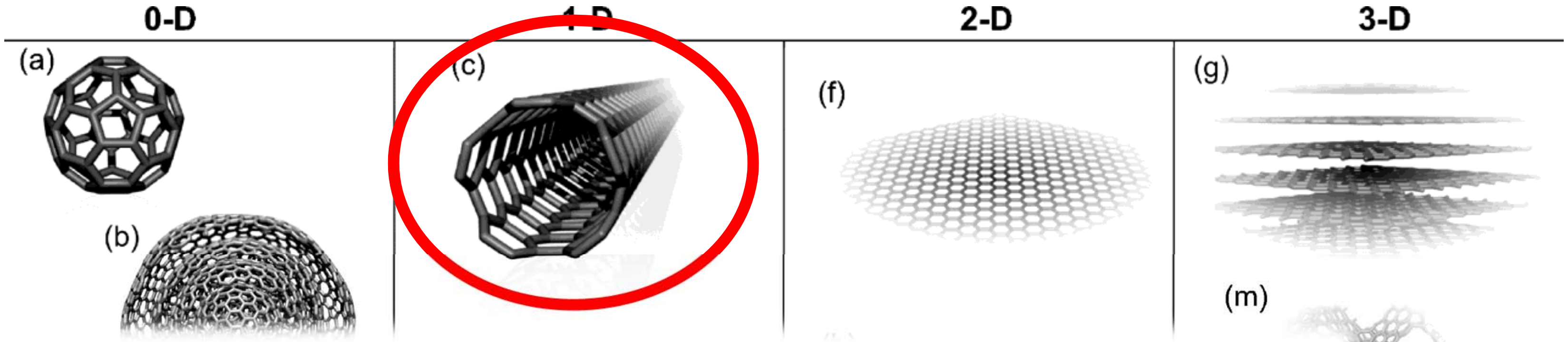
a

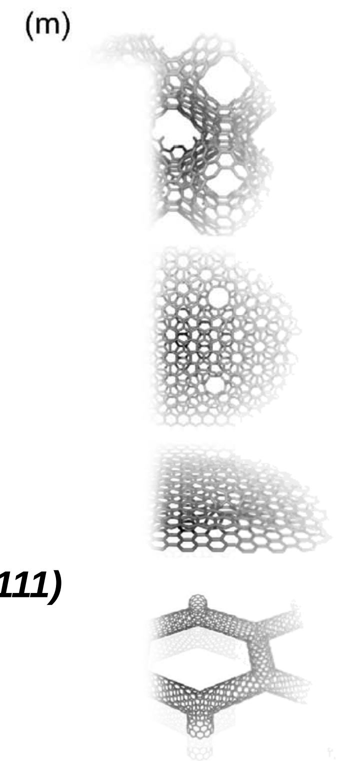


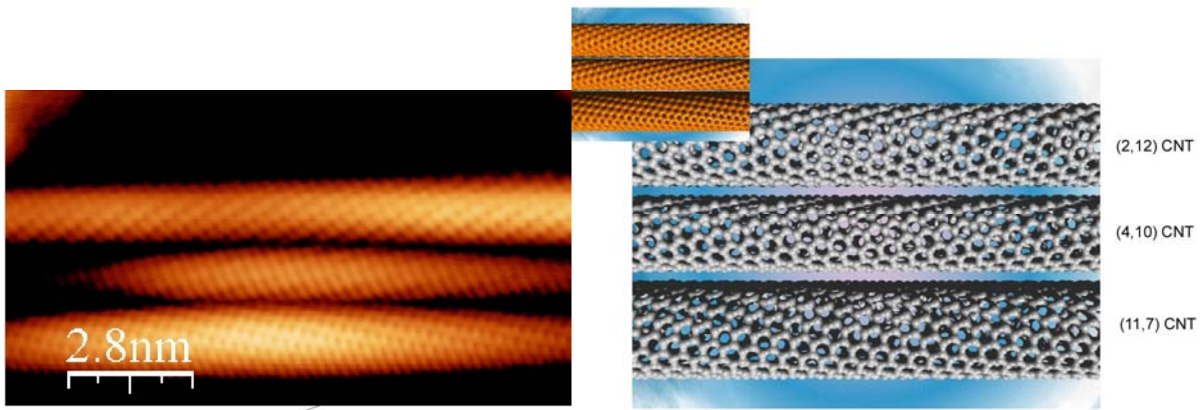
J. Sukegawa, Nat. Chem. 6, 899 (2014)

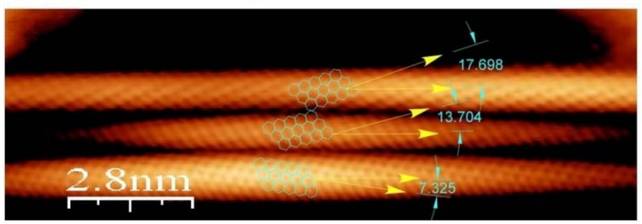
Kohlenstoff Nanoröhrchen

EMPA Materials Science & Technology









Single walled CNT on Au(111)

Gilles Buchs, Thesis Empa 2008

Iijima S., Nature 354, 56–58 (1991)

M. Terrones et al., Nano Today (2010), doi:10.1016/j.nantod.2010.06.010

Sortenreine SWNT

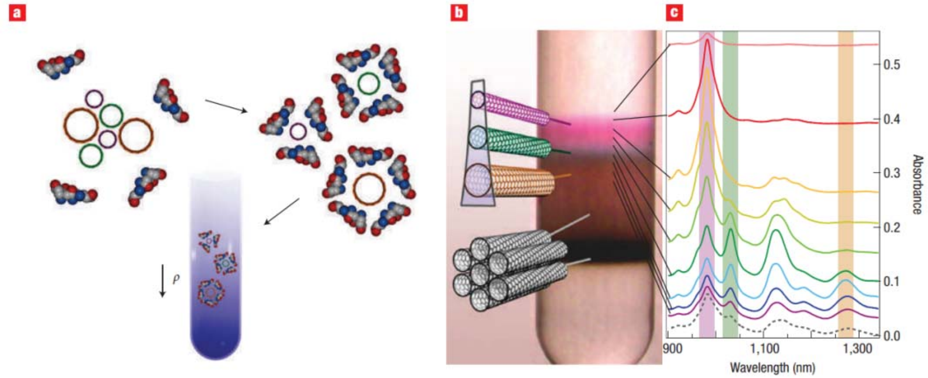
EMPA

Materials Science & Technology

Semiconductor Purity (%)	Price (1 mg)
90	$199
95	$299
98	$449
99	$799

Metallic Purity (%)	Price (1 mg)
70	$199
90	$299
95	$399
98	$699
99	$899

http://www.nanointegris.com/

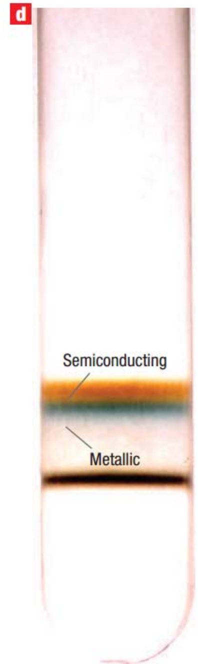


<u>Ultracentrifugation in aqueous solution</u>

The purified SWNT raw material (mixture) is dissolved in water by ultra-sonic treatment and a surfactant (sodium dodecyl sulphate (SDS) and sodium dodecylbenzene sulphonate (SDBS).

The wrapping of the SWNT by the surfactant molecules changes their density as a function of diameter. Ultracentrifugation separates these different fractions.

Selectivity is achieved by wrapping dependence on surfactant mixture and pH. E.g. selective wrapping of semiconducting SWNT.

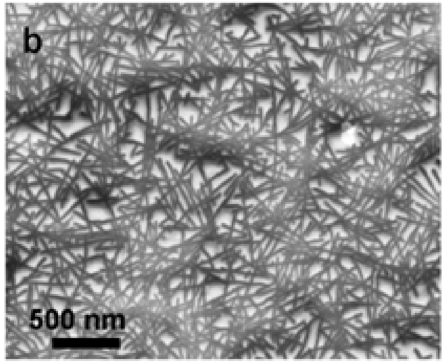


M.S. Arnold et al., Nat. Nanotech. 1, 60 (2006)

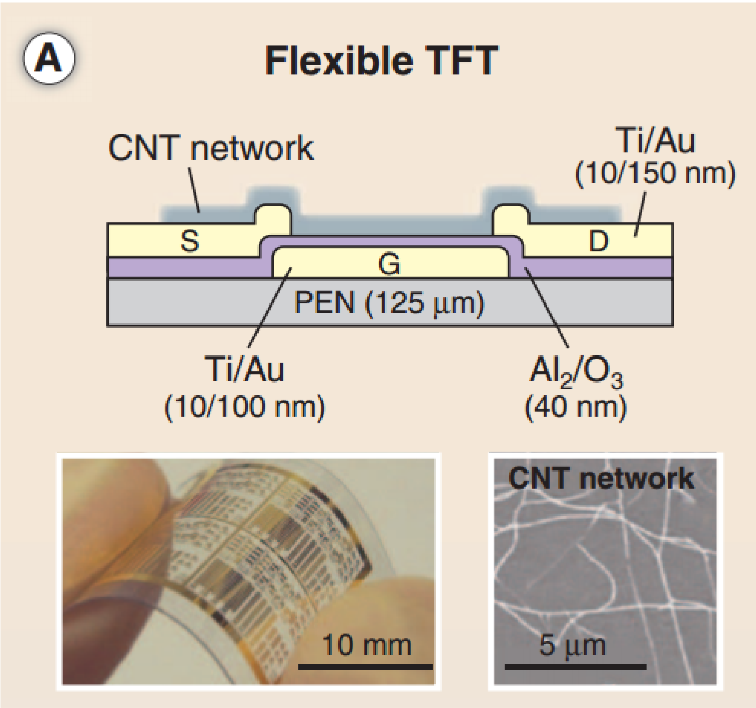
Dünn-Film Transistoren (TFT)

Materials Science & Technology

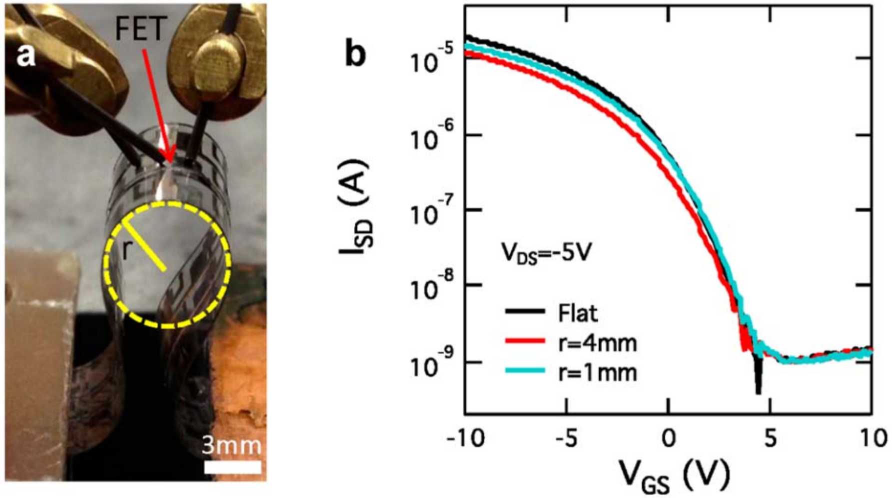
- Large area integration (Displays)
- Low-cost, printable
- Low-frequency, not processor grade
- Signal processing, amplification,
- Memory cells, Sensors, RFID,….



Metallische SWNT würden den aktiven Kanal kurzschliessen und die Transistorwirkung stark reduzieren. Das heisst man möchte hier sortenreine, d.h. nur halbleitende, einwandige CNT haben



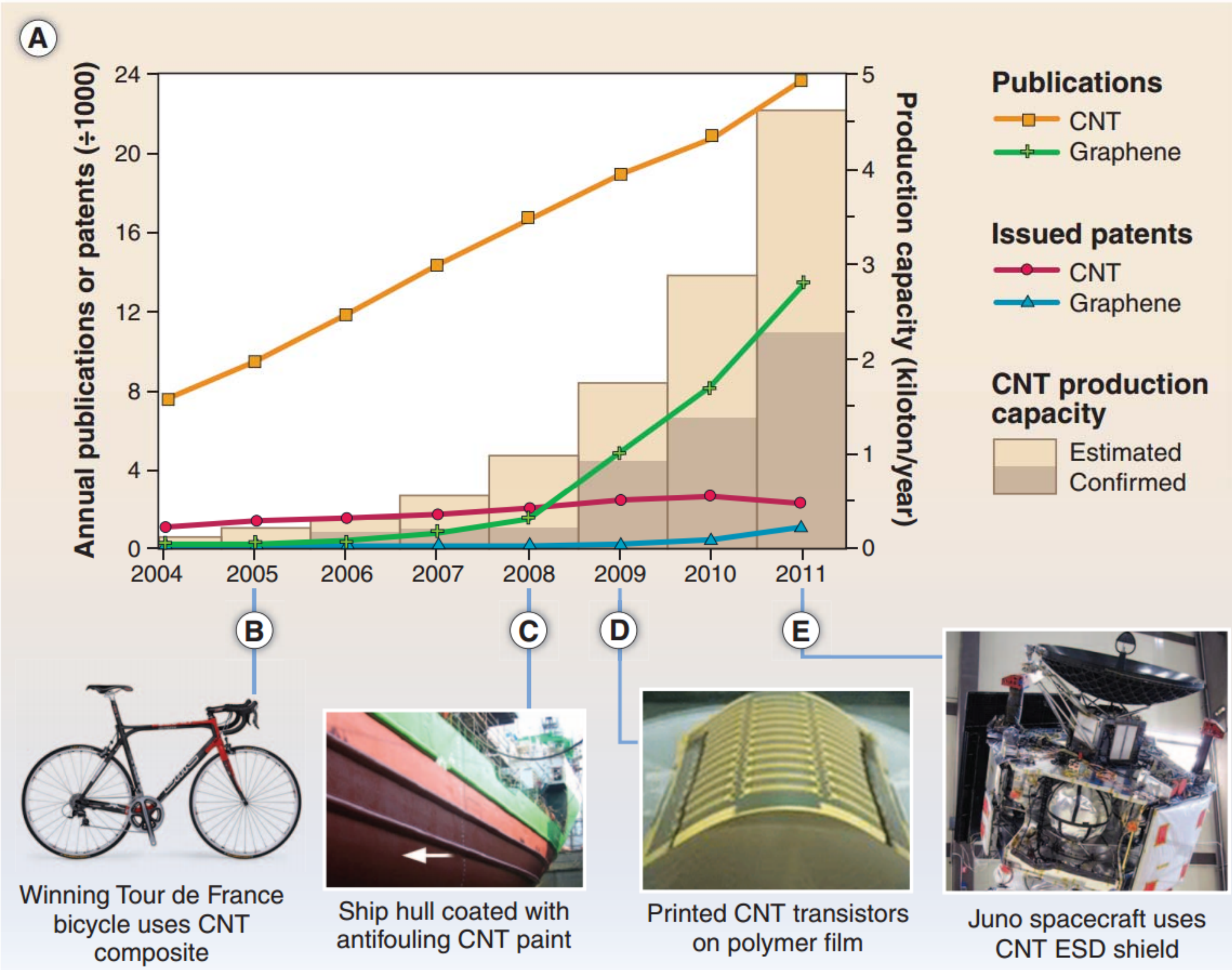
M.F.L. de Volder et al., Science 339, 535 (2013)



P.H. Lau et al., Nano Lett., 2013, 13 (8), pp 3864–3869

Trends in CNT Entwicklung und Anwendung

EMPA Materials Science & Technology



M.F.L. de Volder et al., Science 339, 535 (2013)

Der Globale CNT Markt

EMPA
Materials Science & Technology

	Large-volume applications	Limited-volume applications	Key attributes
Present	Sporting goods such as golf shafts, tennis rackets, baseball bats etc., battery electrode additives, plastics additives and masterbatches, fuel line systems	Battery electrodes, boat hulls & decks, wind turbine blades, prepregs, scanning probe tips, sensors, catheters, membrane filters, flat panel displays, textiles, printing & packaging	Excellent mechanical and electrical conductivity properties, compatibility, high surface area (~1000 m²/g), excellent chemical stability in acidic environments, distinguished optoelectronic properties, insensitivity to electromigration, excellent thermal conductivities and semiconducting properties
Near term (less than five years)	Supercapacitor electrodes, transparent conducting films, field emission displays, LCDs and OLED-based displays, fuel cell electrodes, inks for printing, adhesives	Electromechanical memory device, hydrogen-storage electrodes, biosensors, multitip array X-ray sources, probe array test systems, brush contacts, thermal-management systems	
Long term (beyond five years)	Power transmission cables, structural composites applications for aerospace and automobile, photovoltaic devices	Field-Effect Transistors (FET), interconnects, flexible electronics, drug-delivery systems	

Markt Volumen 2011: ***670 Mio. $***

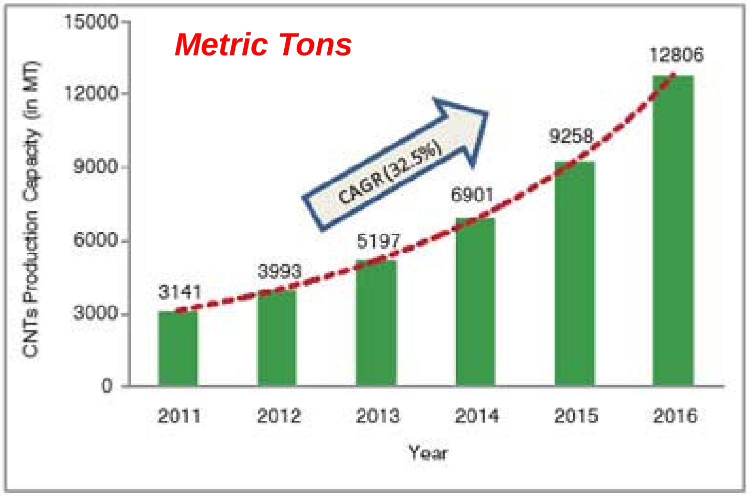
MWNT: ***630 Mio. $***

SWNT: ***40 Mio. $***

Markt Volumen 2014: ***ca. 950 Mio. $***

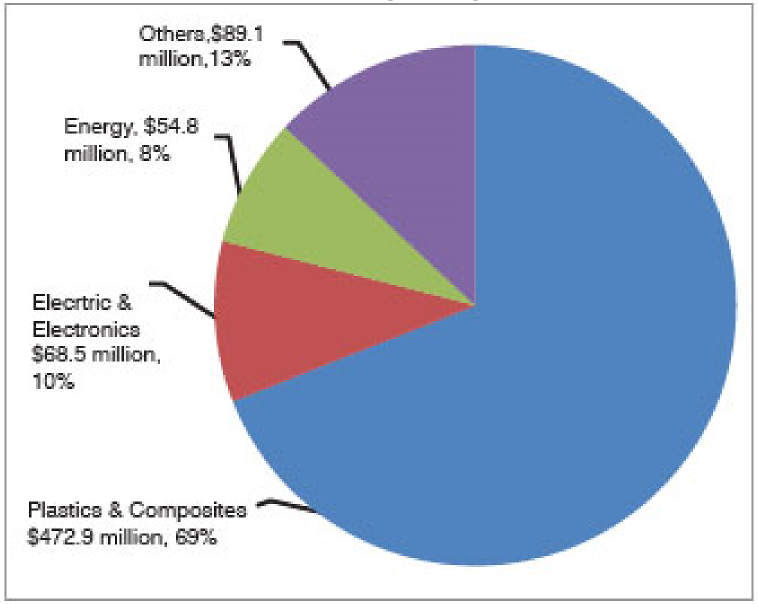
Zuwachsrate: ***ca. 10-15 %/p.a.***

Produktion

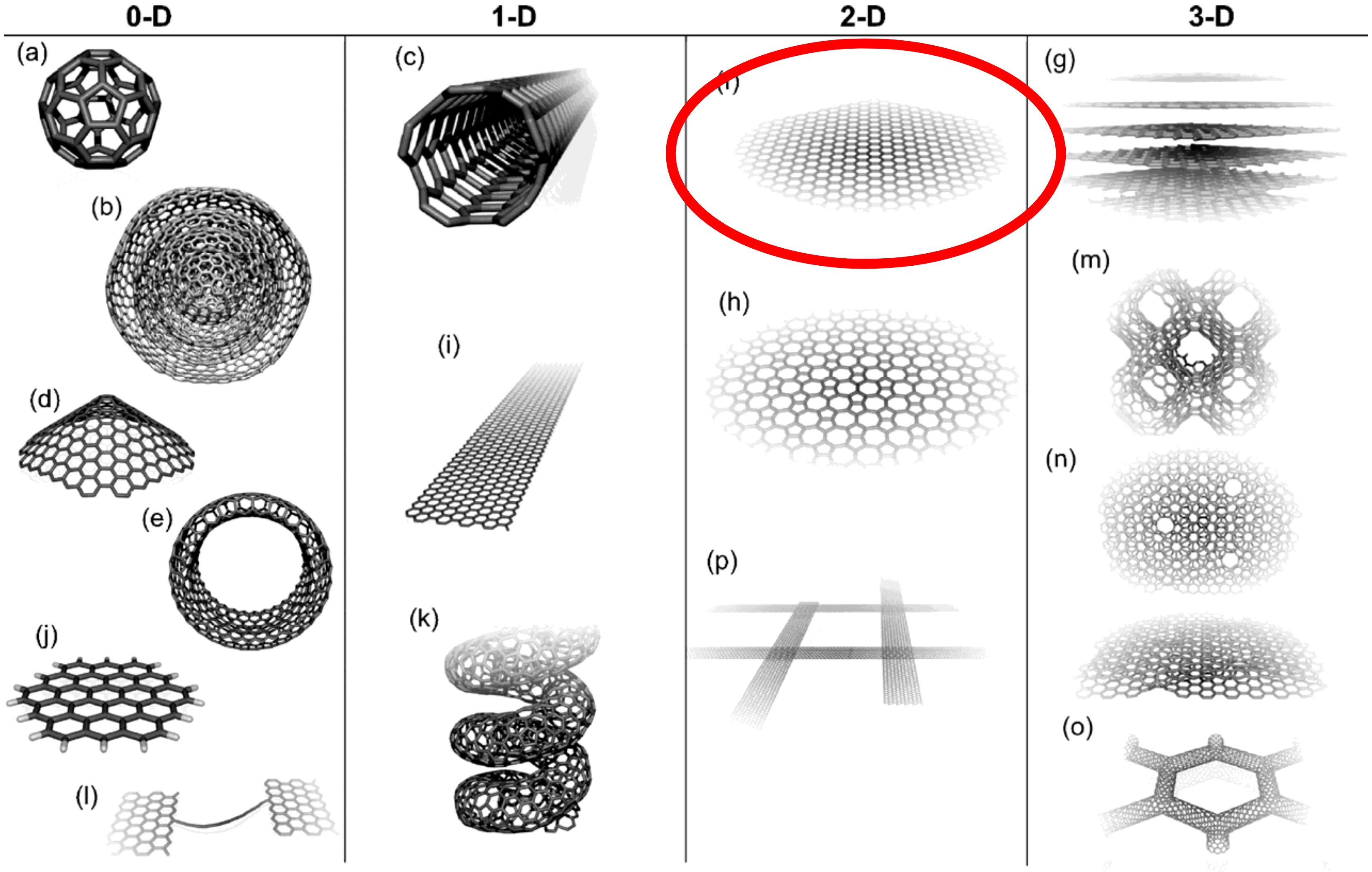


http://www.nanowerk.com/spotlight/spotid=23118.php

Umsatz in Anwendungssegmenten



Nano/Low dimensional carbon materials



M. Terrones et al., Nano Today (2010), doi:10.1016/j.nantod.2010.06.010

Anwendungsfelder von Graphen

EMPA
Materials Science & Technology

Transparente Elektroden

- Bildschirme LCD, OLED, e-Paper
- Touch-Screens
- Org. oder Farbstoff-Solarzellen
- Flexible Bildschirme
- Grossflächige LED/OLED Beleuchtung

Elektroden hoher Oberfläche

- Elektrolytische Super-Kondensatoren
- Li-Ionen Batterien
- Elektroden für Solarzellen
- Trägermaterial in Brennstoffzellen

Composite

- Erhöhung der mechanischen Belastbarkeit von Polymeren- oder Verbundwerkstoffen
- Leitfähige Polymere für elektromagnetische Abschirmung oder gegen statische Aufladung
- Elektroden für Solarzellen
- Verbesserung der Biokompatibilität

Printable Electronics

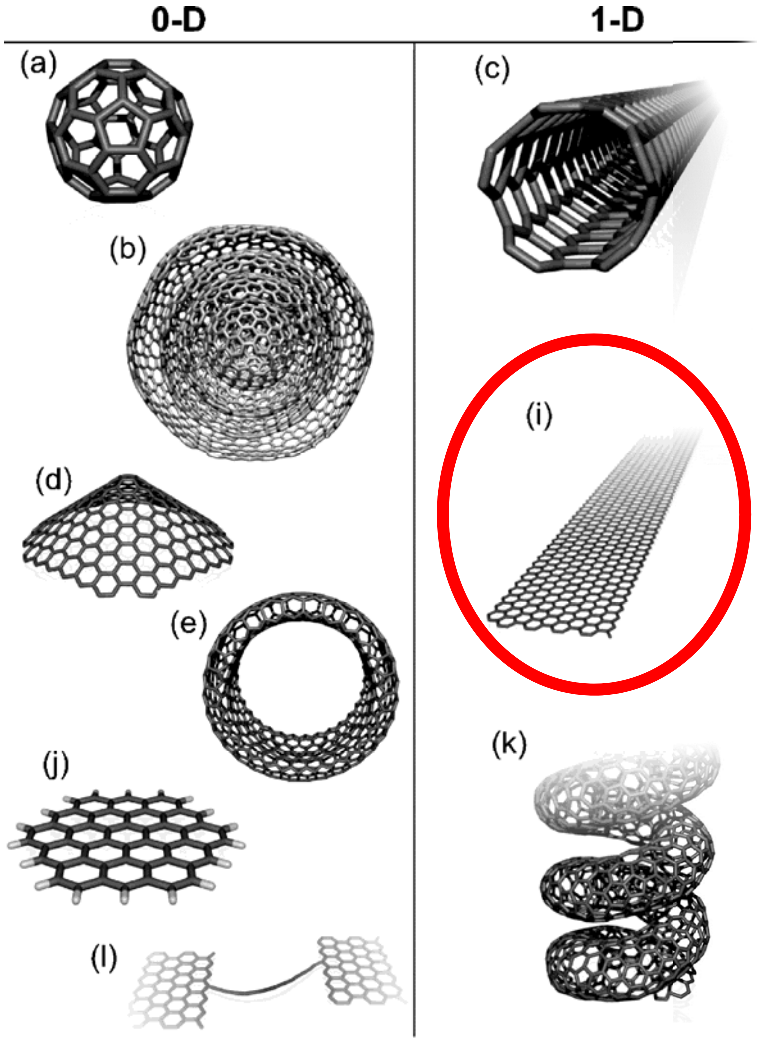
- Leitfähige Pasten und Suspensionen
- Antistatische Beschichtungen
- RF-ID Tags
- Low cost Elektronic
- Flexible Bildschirme

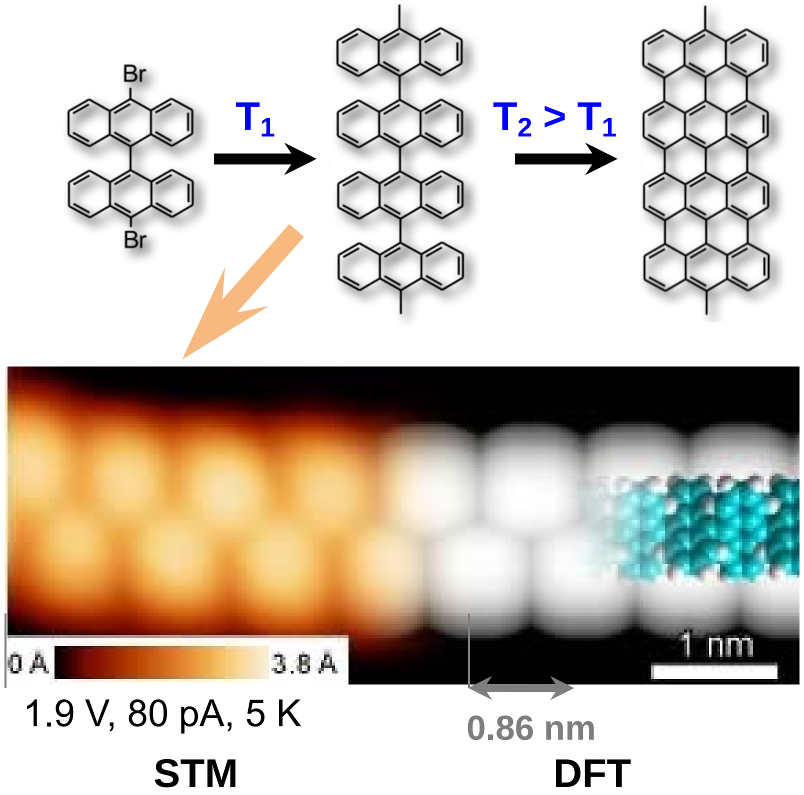
Analog-Digital Elektronik

- Ultra-schnelle Transistoren
- THz Analog Elektronik
- Sensoren
- Opto-Elektronische Komponenten

- Nano-Elektromechanische Komponenten
- Feuchtigkeits- und Gas-Barriere Beschichtungen
- ….

Nano/Low dimensional carbon materials

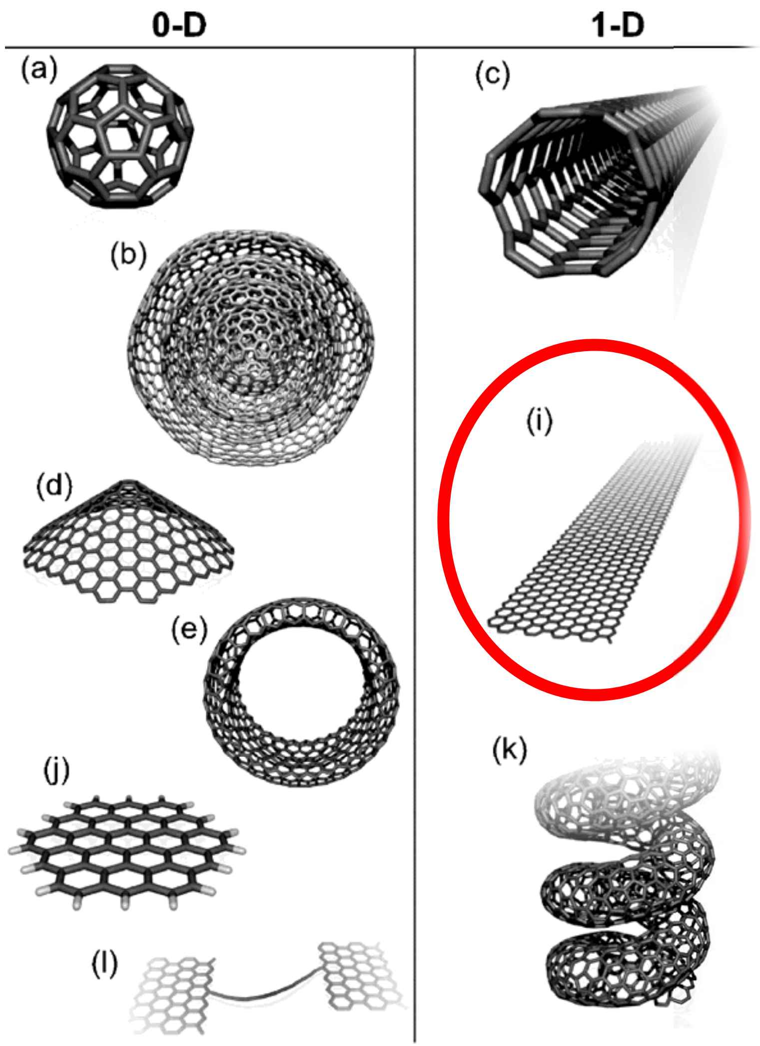




M. Terrones et al., Nano Today (2010), doi:10.1016/j.nantod.2010.06.010

Nano/Low dimensional carbon materials

EMPA
Materials Science & Technology

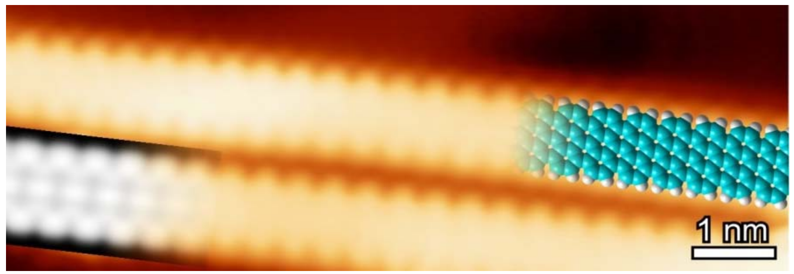


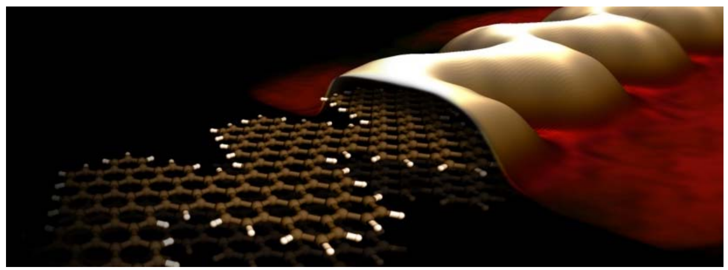

nature Vol 466 | 22 July 2010 | doi:10.1038/nature09211

LETTERS

Atomically precise bottom-up fabrication of graphene nanoribbons

Jinming Cai[1]*, Pascal Ruffieux[1]*, Rached Jaafar[1], Marco Bieri[1], Thomas Braun[1], Stephan Blankenburg[1], Matthias Muoth[2], Ari P. Seitsonen[3,4], Moussa Saleh[5], Xinliang Feng[5], Klaus Müllen[5] & Roman Fasel[1,6]

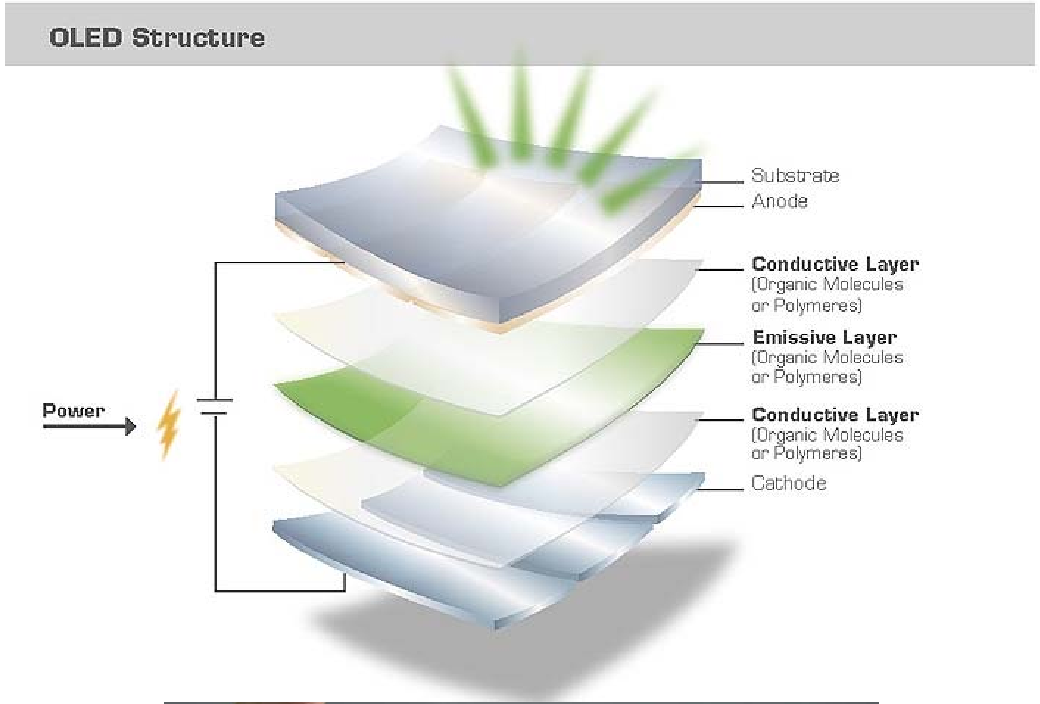




M. Terrones et al., Nano Today (2010), doi:10.1016/j.nantod.2010.06.010

Flexible Electronics
z.B. Organic Light Emitting Diode (OLED)

EMPA Materials Science & Technology



Substrate:
- Glass
- Polymer
- Metall
- Papier

Zwischenschichten:
- **Barrieren / Verkapselung**
- Haftvermittler
- **Elektronische Angleichung**

Aktive Schichten:
- **Halbleiter/Transistor**
- Lichtemission
- **Widerstand**
- **Sensoraktiv**
- **Photovoltaik**

Elektroden:
- **Leiterbahnen**
- **Anode/Kathoden**

Dielektrika:
- Isolation
- Kondensator

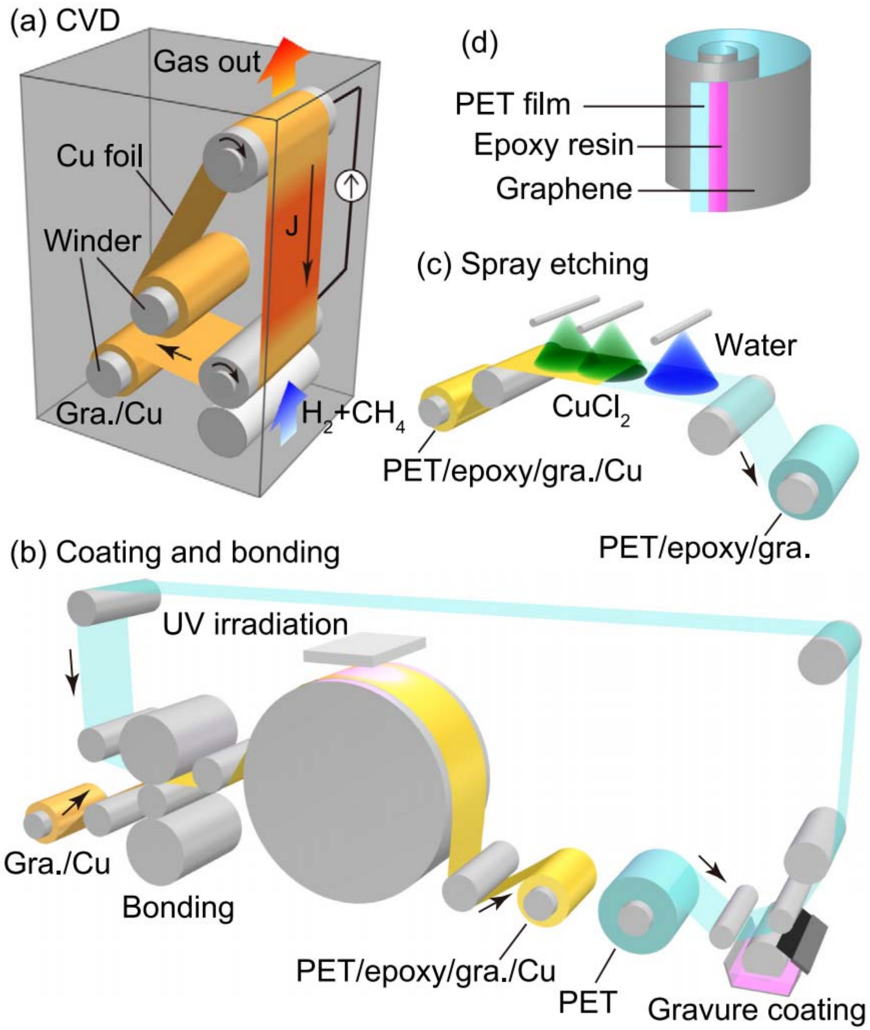
Grossflächige Graphen Produktion

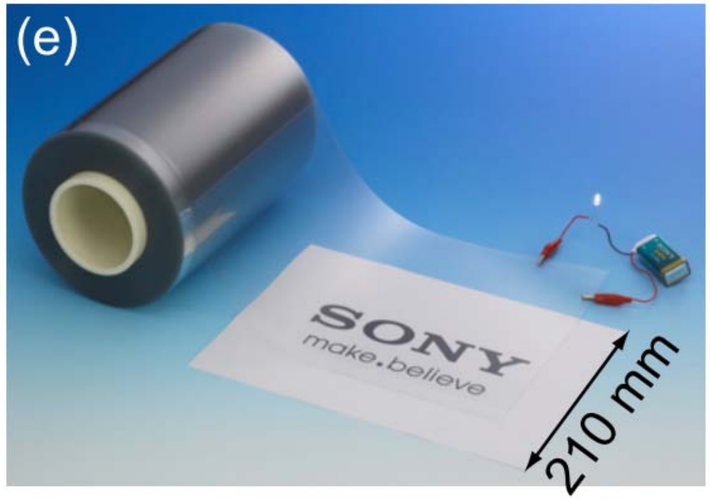
Materials Science & Technology

APPLIED PHYSICS LETTERS **102**, 023112 (2013)

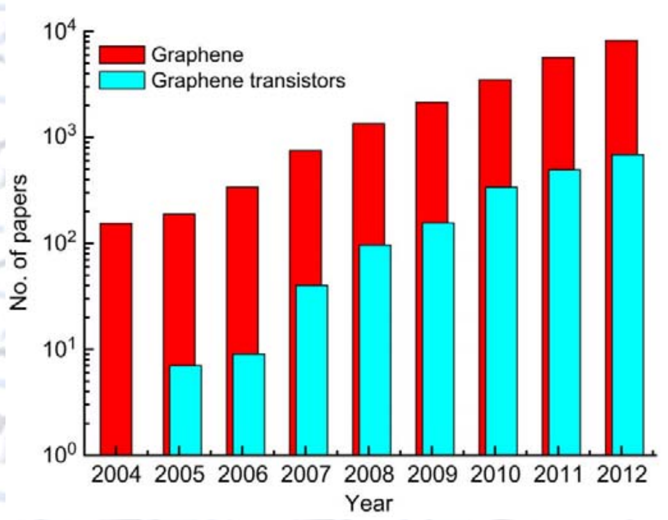
Production of a 100-m-long high-quality graphene transparent conductive film by roll-to-roll chemical vapor deposition and transfer process

Toshiyuki Kobayashi,[a] Masashi Bando, Nozomi Kimura, Keisuke Shimizu, Koji Kadono, Nobuhiko Umezu, Kazuhiko Miyahara, Shinji Hayazaki, Sae Nagai, Yukiko Mizuguchi, Yosuke Murakami, and Daisuke Hobara
Advanced Materials Laboratories, Sony Corporation, Atsugi-Shi, Kanagawa 243-0014, Japan

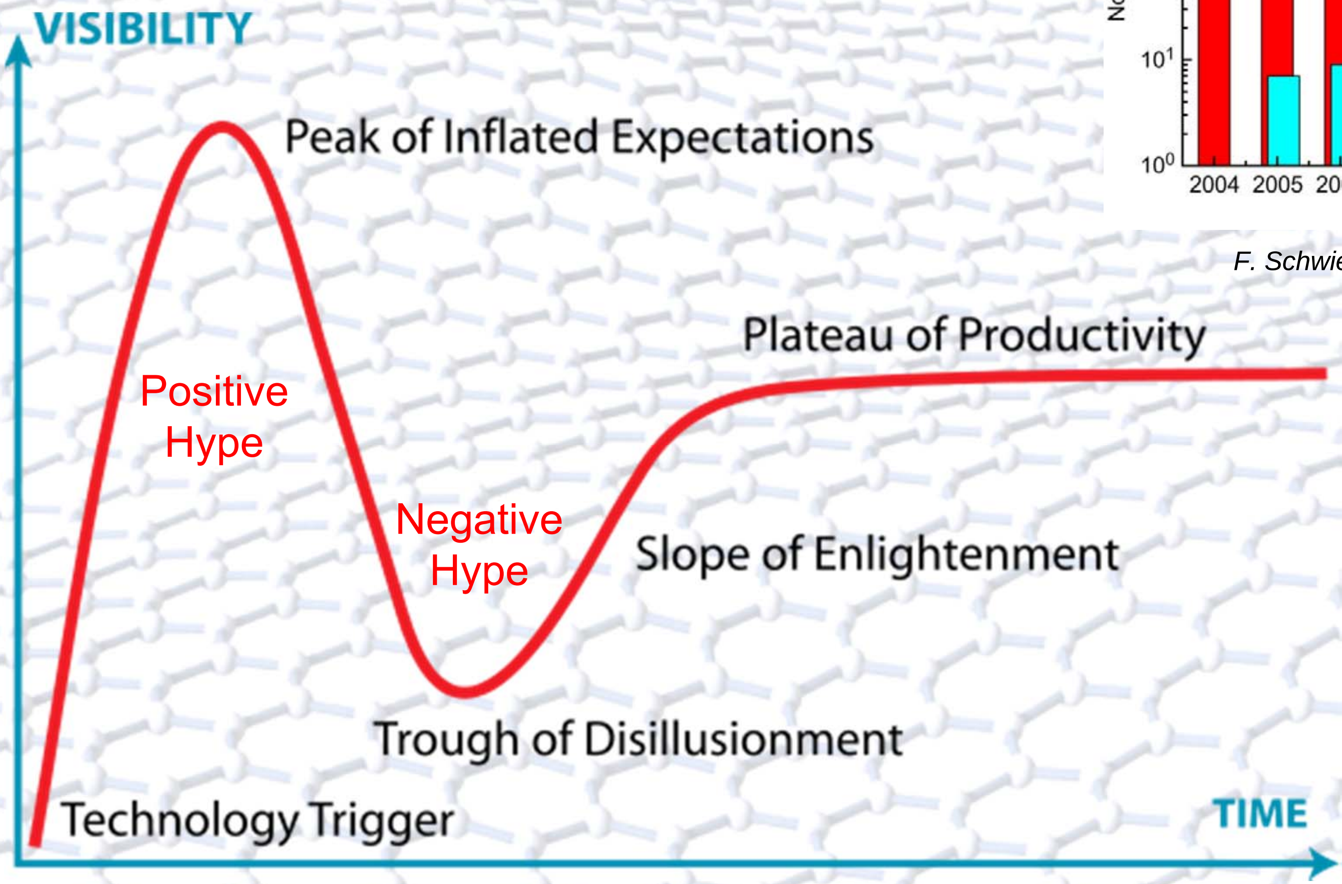




Graphen: Hype oder Hoffnung?



F. Schwierz, Proc. IEEE, 101, 7, 1567 (2013)



adapted from: http://en.wikipedia.org/wiki/Hype_cycle

EMPA
Materials Science & Technology

Danke für die Aufmerksamkeit