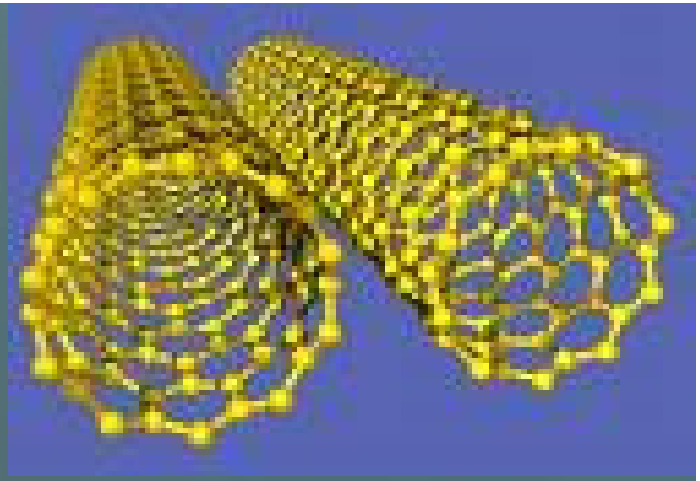


CARBON NANOTUBES for PHOTONICS

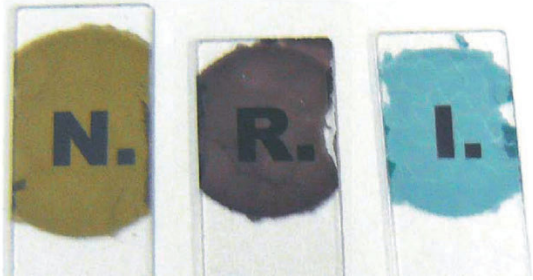
Elena Obraztsova

A.M. Prokhorov General Physics Institute, RAS

elobr@kapella.gpi.ru

A breaking new of today!!!:

Nanotube of different diameters



K.Yanagi, Y. Miyata, and H. Kataura,

Appl. Phys. Express 1(2008) 034003.

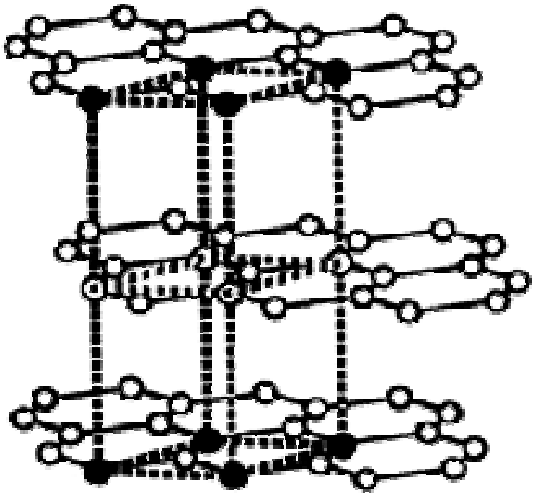
OUTLINE

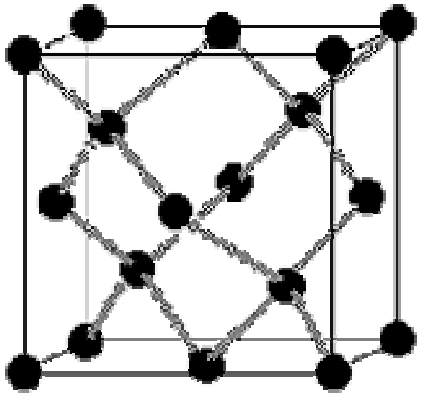
Single-wall carbon nanotubes:

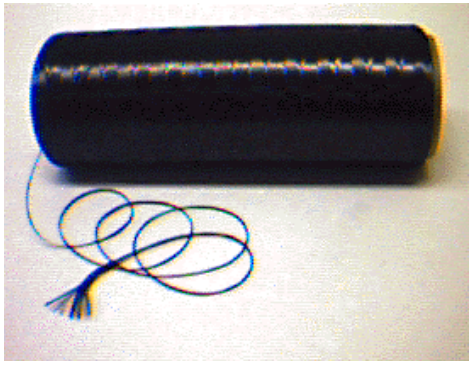
1. A few historical facts.
2. Structure and unique electronic properties.
3. A way to the optical quality.
4. UV-VIS-NIR optical absorption and photoluminescence.
5. Optical non-linearity.
6. Application: Passive mode locking in solid state lasers.
7. Prospectives.

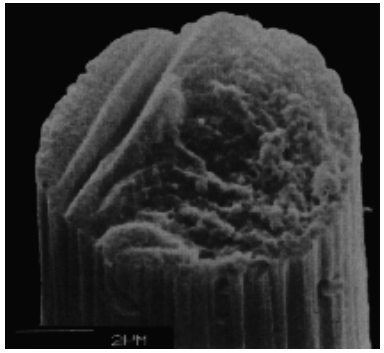
CARBON

Graphite ← CARBON → **Diamond**







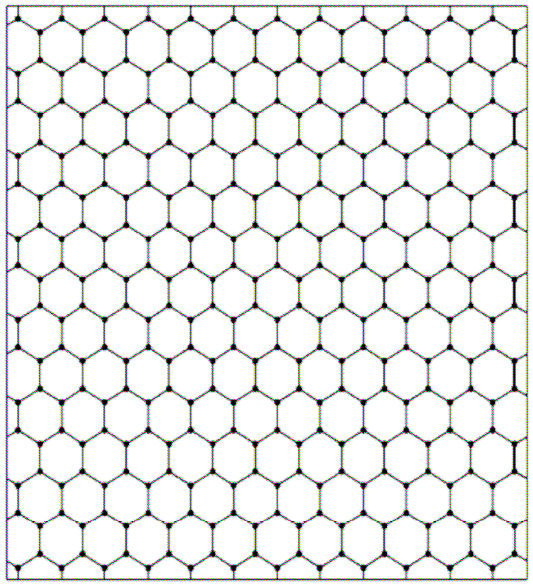


order
1 µm

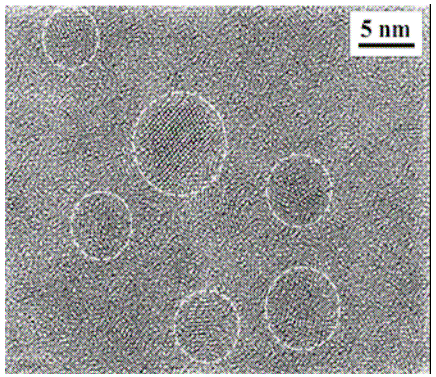
30 nm

disorder
3 nm

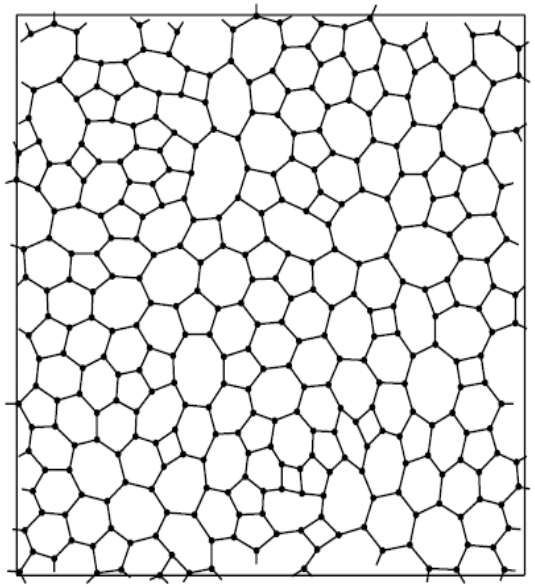
Single crystal



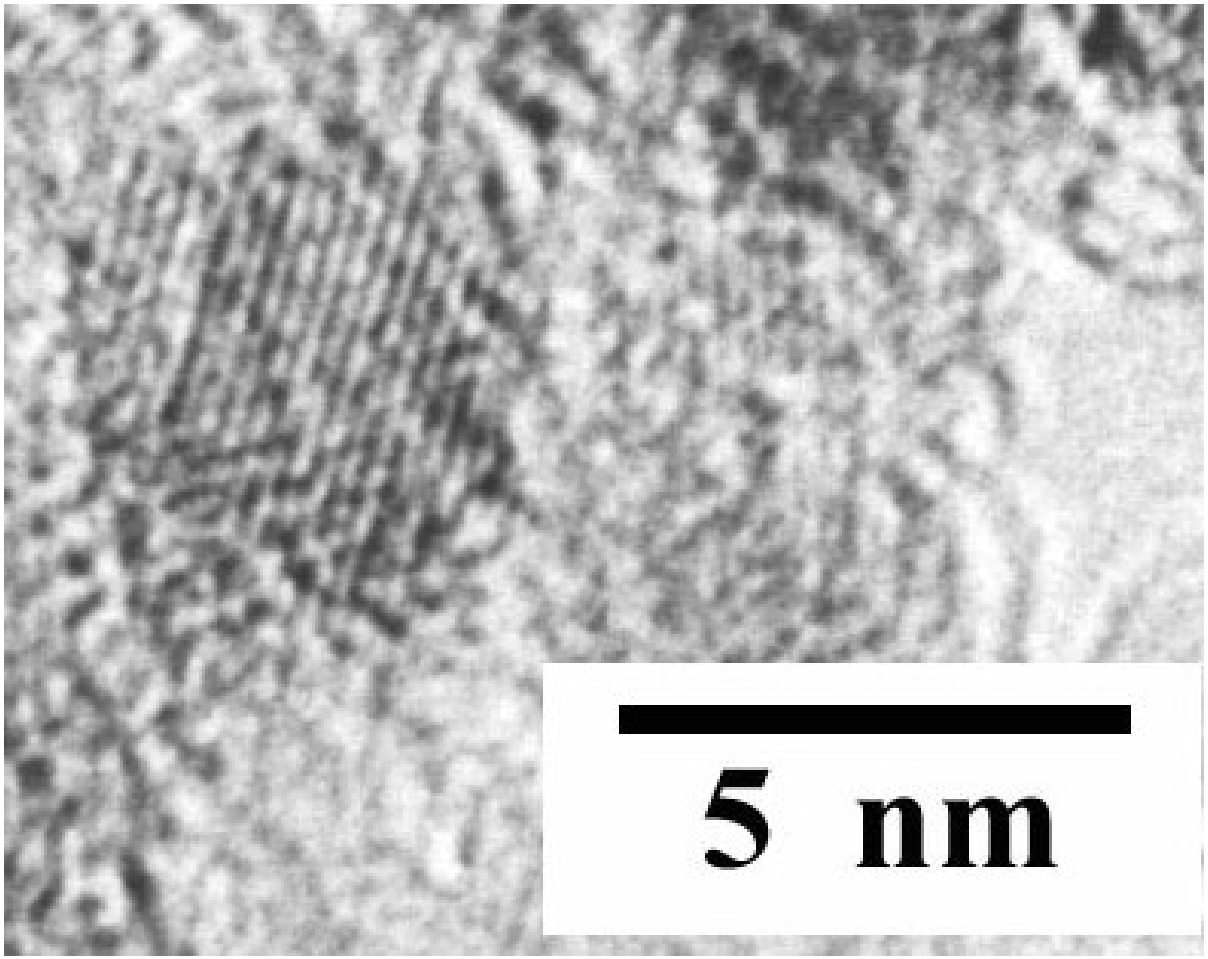
Nanocrystal



Amorphous state



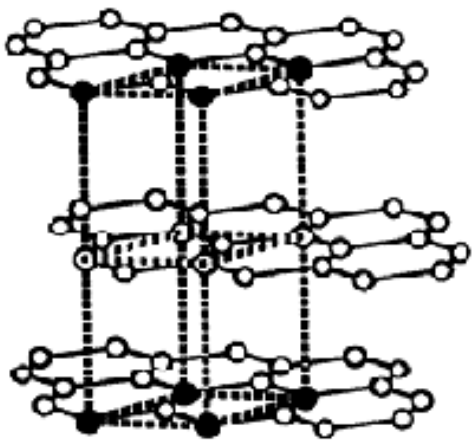
Diamond nanoparticles – 0-dimensional diamond



Obraztsova et al., *Carbon 36 (1998) 821*

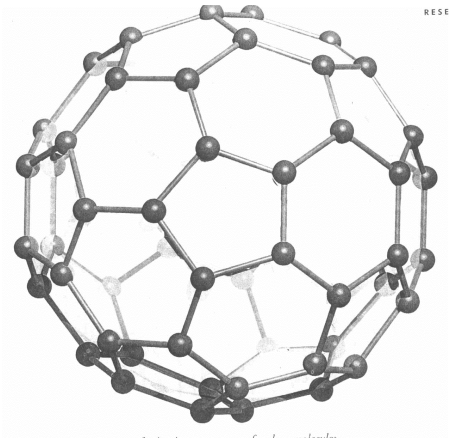
1µm ***Self-organization*** → **3 nm**

graphite

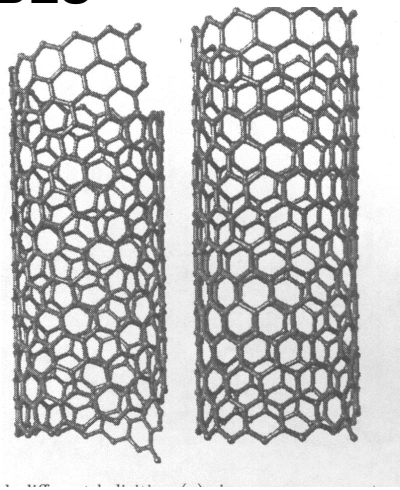


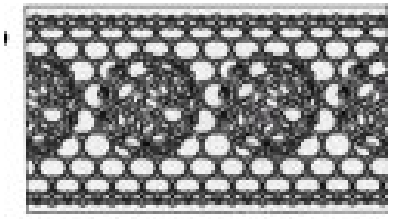
ONIONS

FULLERENES



SINGLE-WALL NANOTUBES





PEAPODS

History

The Nobel Prize in Chemistry 1996

"for their discovery of fullerenes"

http:// www.nobel.se

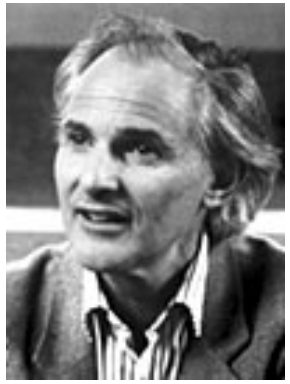
Robert F. Curl Jr.

1/3 of the prize

USA

Rice University
Houston, TX, USA

b. 1933



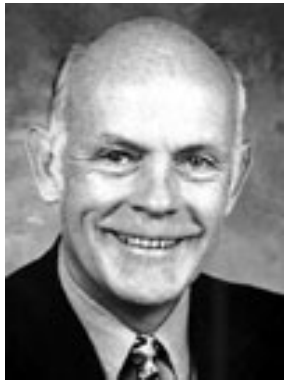
Sir Harold W. Kroto

1/3 of the prize

United Kingdom

University of Sussex
Brighton, United Kingdom

b. 1939



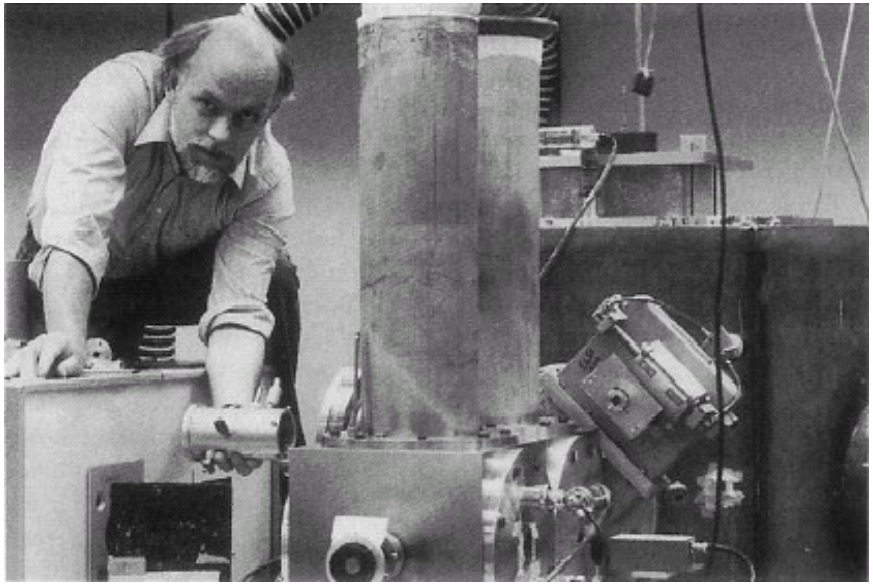
Richard E. Smalley

1/3 of the prize

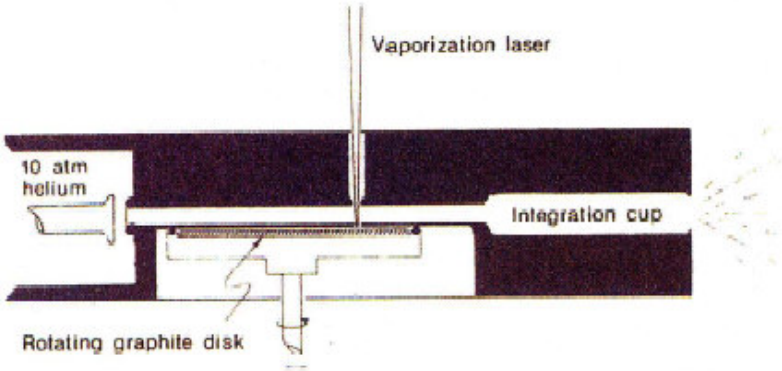
USA

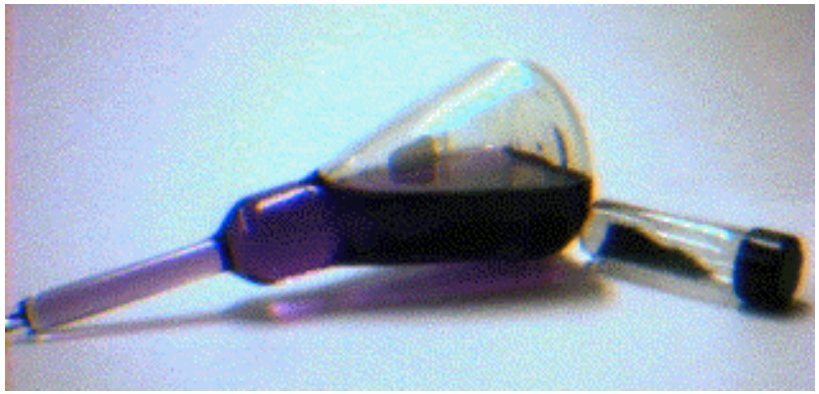
Rice University
Houston, TX, USA

b. 1943

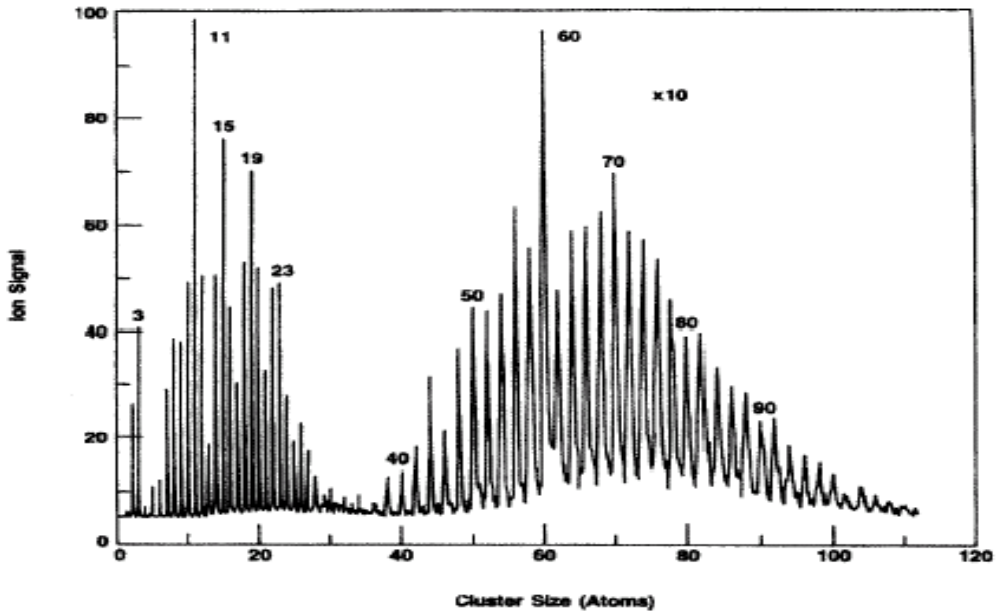


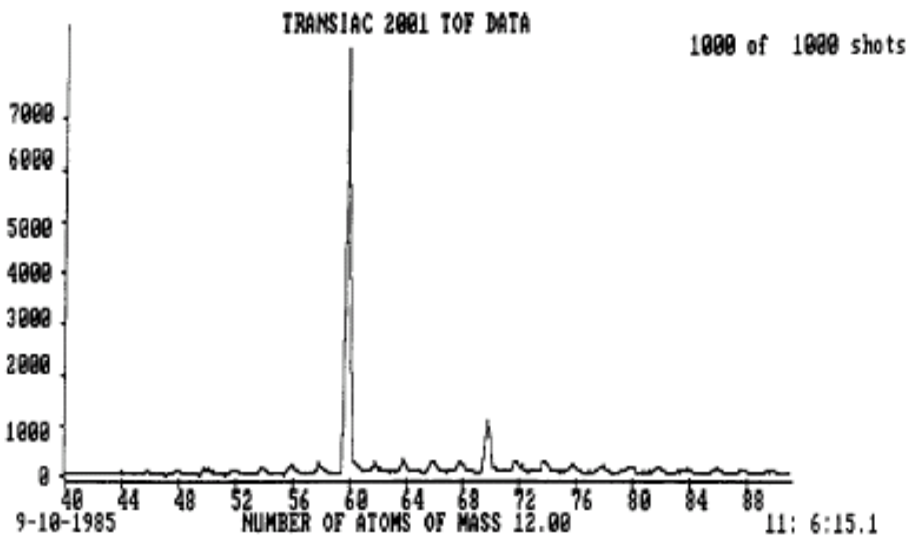
A first chamber for laser ablation synthesis of carbon clusters





Nature 318 (1985) 162





Mass-spectrometry of carbon clusters, formed via the laser ablation of graphitic target

C_{60}- buckyball

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

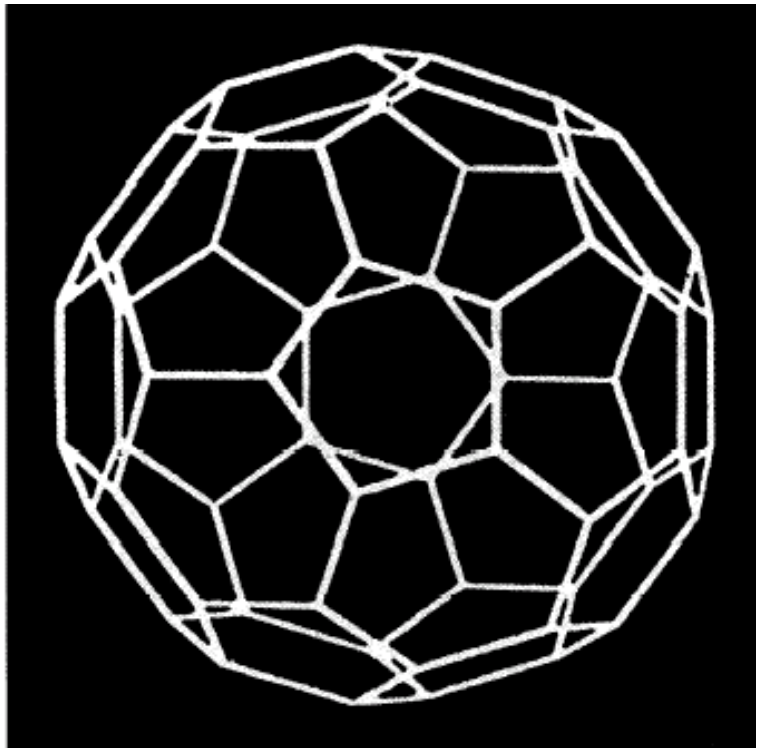
During experiments aimed at understanding the mechanisms by which long-chain carbon molecules are formed in interstellar space and circumstellar shells[1], graphite has been vaporized by laser irradiation, producing a remarkably stable cluster consisting of 60 carbon atoms. Concerning the question of what kind of 60-carbon atom structure might give rise to a superstable species, we suggest a truncated icosahedron, a polygon with 60 vertices and 32 faces, 12 of which are pentagonal and 20 hexagonal. This object is commonly encountered as the football shown in Fig. 1. The C_{60} molecule which results when a carbon atom is placed at each vertex of this structure has all valences satisfied by two single bonds and one double bond, has many resonance structures, and appears to be aromatic.

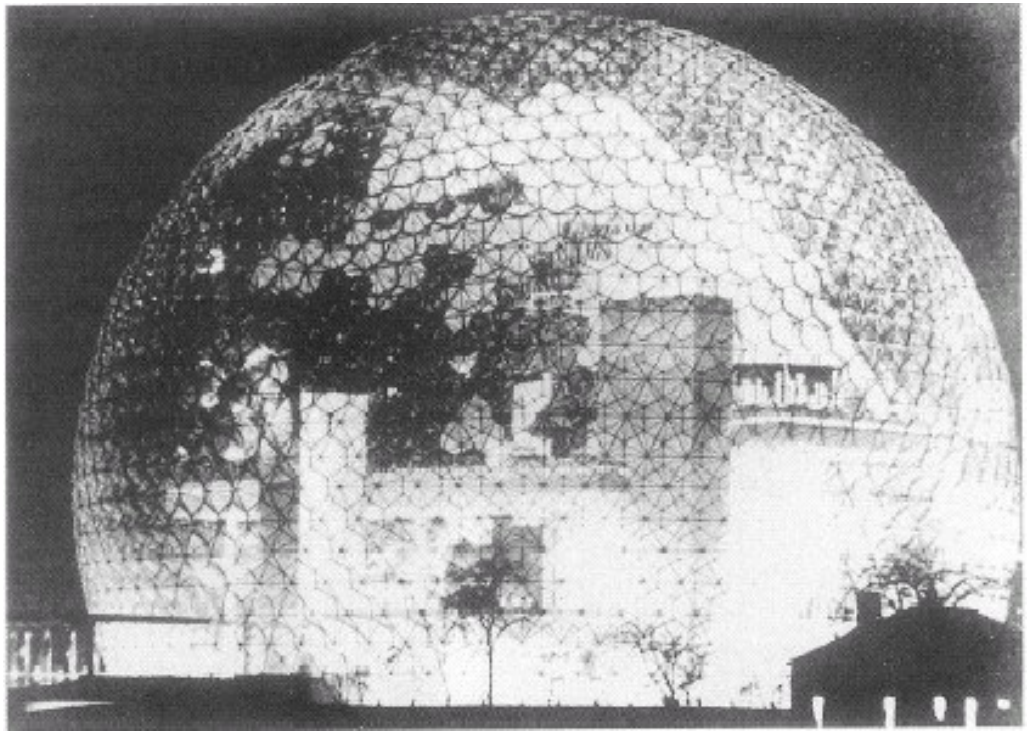
Fig. 1 A football (in the United States, a soccerball) on Texas grass. The C_{60} molecule featured in this letter is suggested to have the truncated icosahedral structure formed by replacing each vertex on the seams of such a ball by a carbon atom.

graphite fused six-membered ring structure. We believe that the distribution in Fig. 3c is fairly representative of the nascent distribution of larger ring fragments. When these hot ring clusters are left in contact with high-density helium, the clusters equilibrate by two- and three-body collisions towards the most stable species, which appears to be a unique cluster containing 60 atoms.

When one thinks in terms of the many fused-ring isomers with unsatisfied valences at the edges that would naturally arise

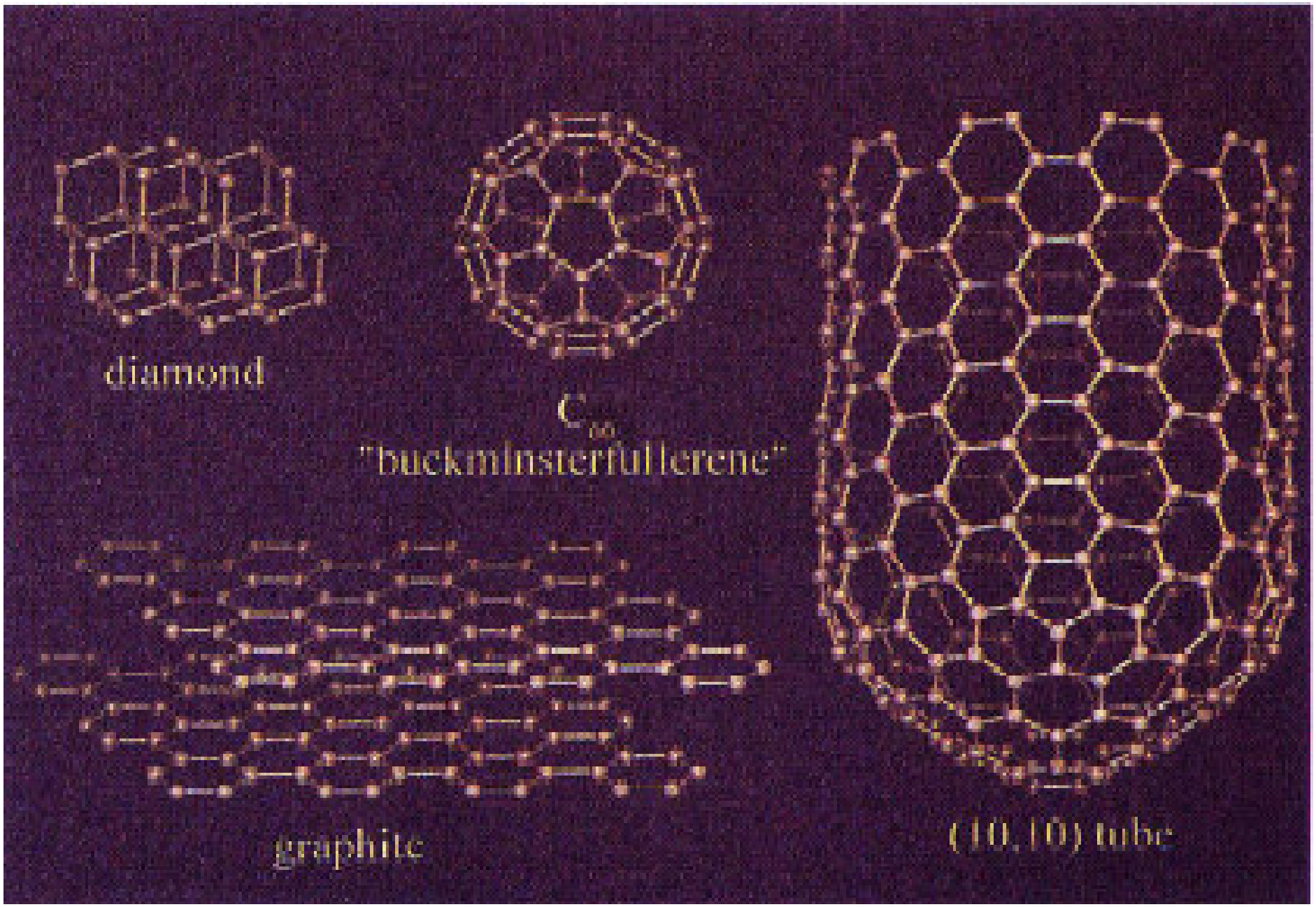
Nature 318 (1985) 162





C_{60} molecule

A geodesic dome built by the architect Richard Buckminster Fuller for the exhibition EXPO Montreal, 1967


diamond
C_{60}
"buckminsterfullerene"
graphite
(10,10) tube

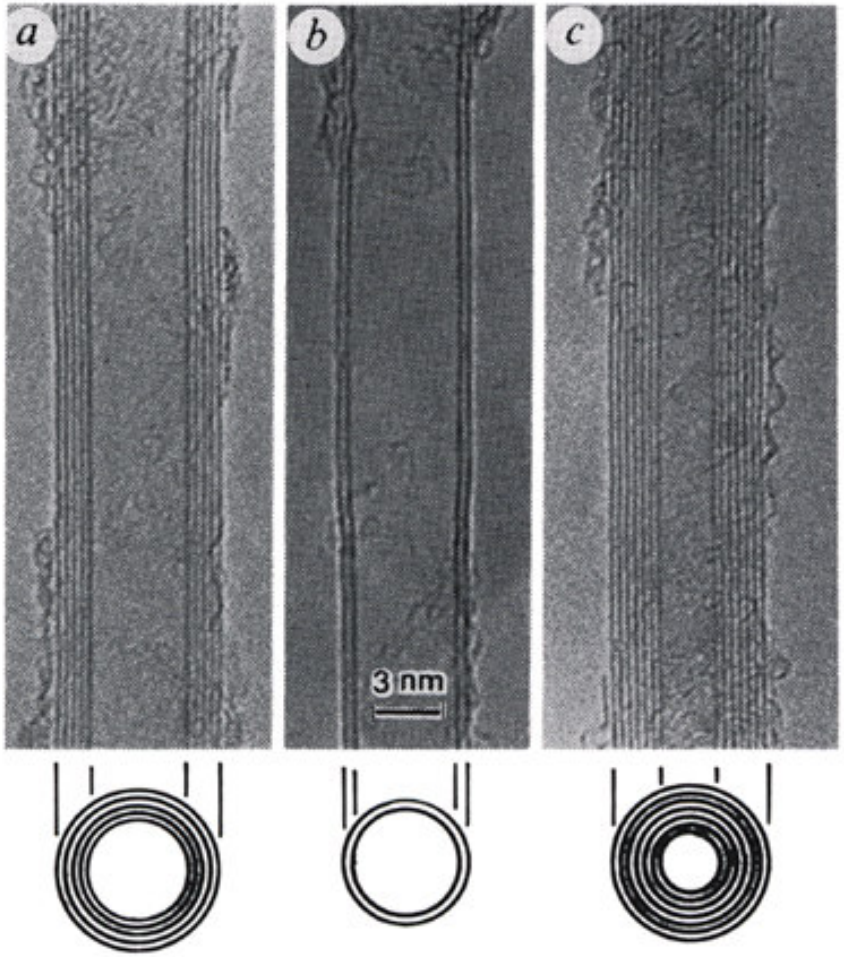
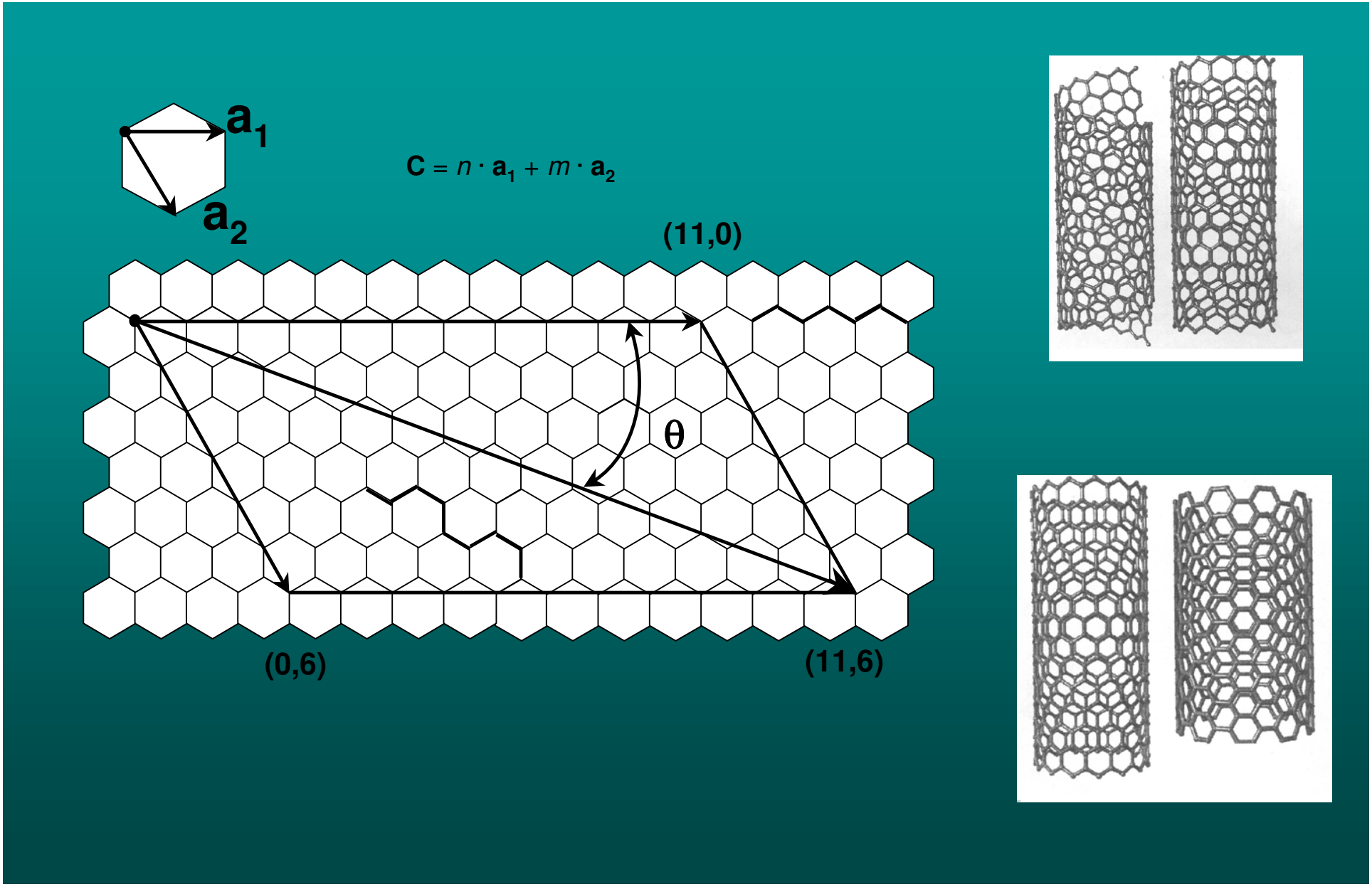


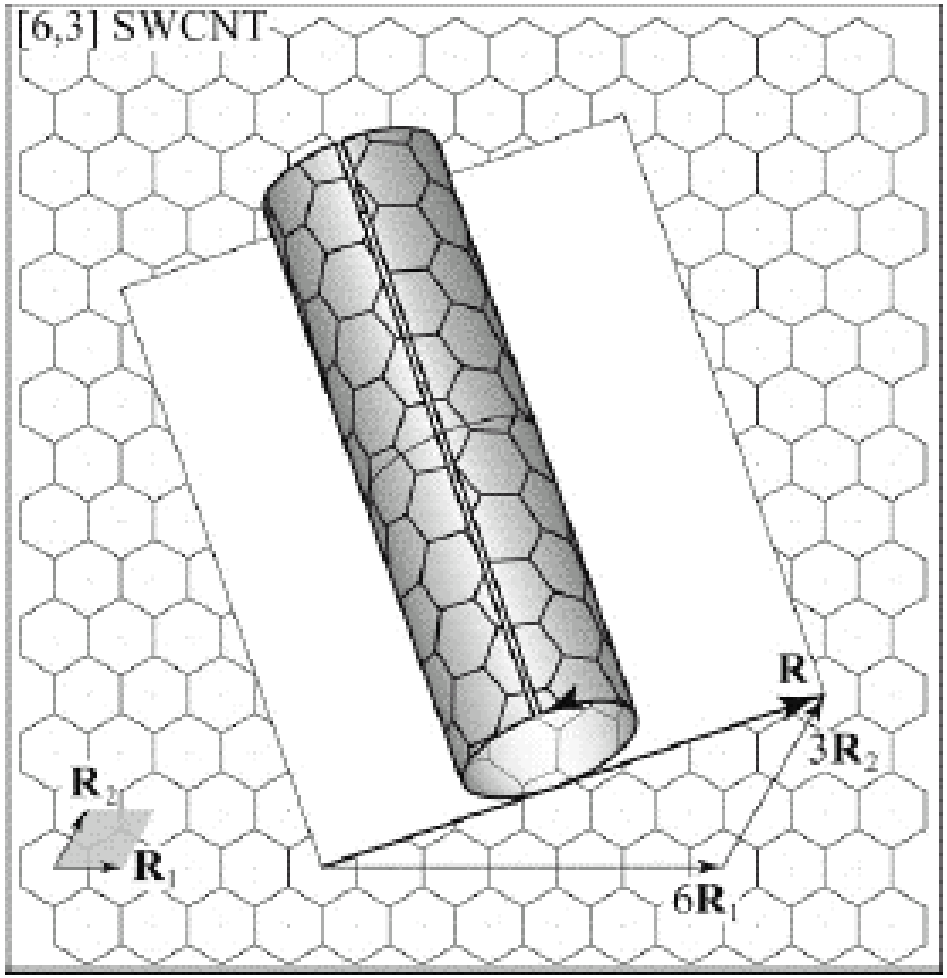
FIG. 1 Electron micrographs of microtubules of graphitic carbon. Parallel dark lines correspond to the (002) lattice images of graphite. A cross-section of each tubule is illustrated. *a*, Tube consisting of five graphitic sheets, diameter 6.7 nm. *b*, Two-sheet tube, diameter 5.5 nm. *c*, Seven-sheet tube, diameter 6.5 nm, which has the smallest hollow diameter (2.2 nm).

S.Iijima, Nature 354 (1991) 56



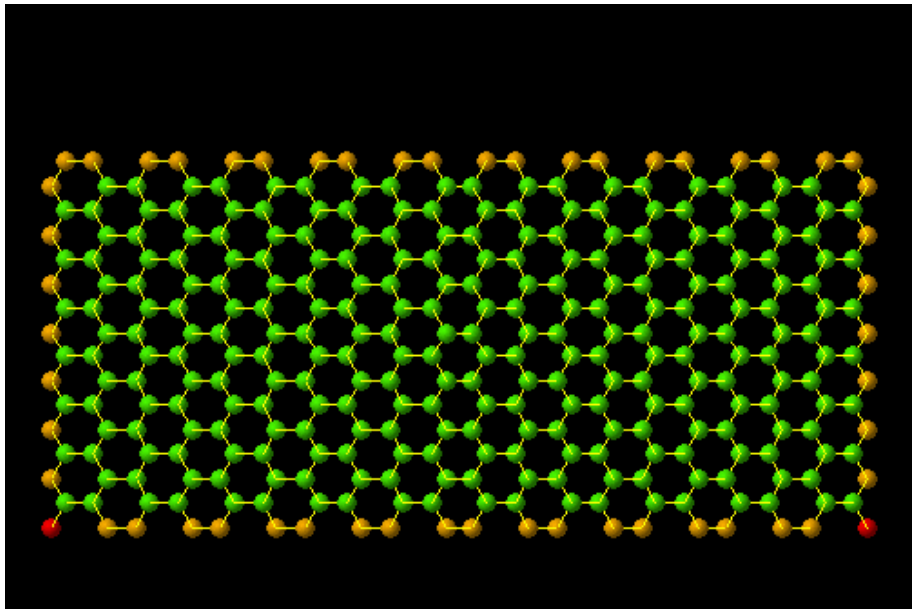
Formation of carbon nanotubes of different geometry

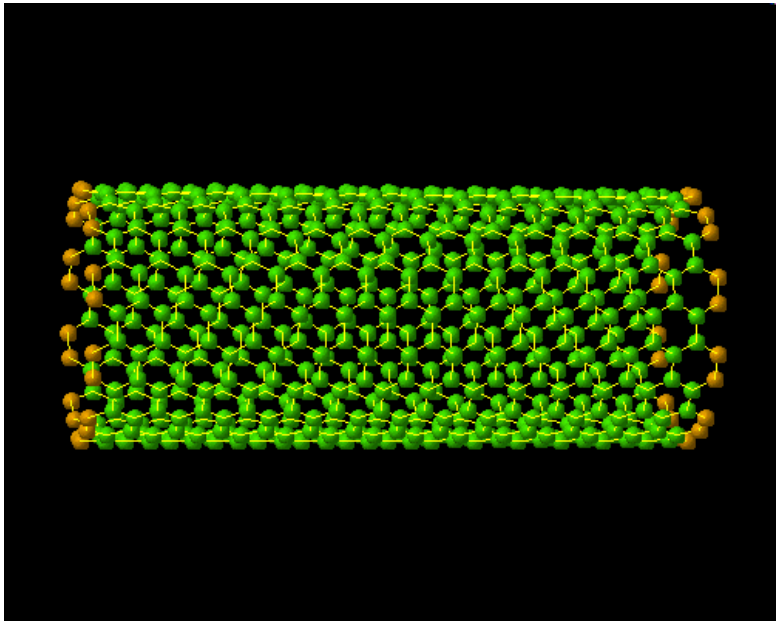
J. Phys. Chem. B109 (2005)52



Formation of single-wall nanotube (6,3) from the graphene sheet

Formation of a single-wall nanotube

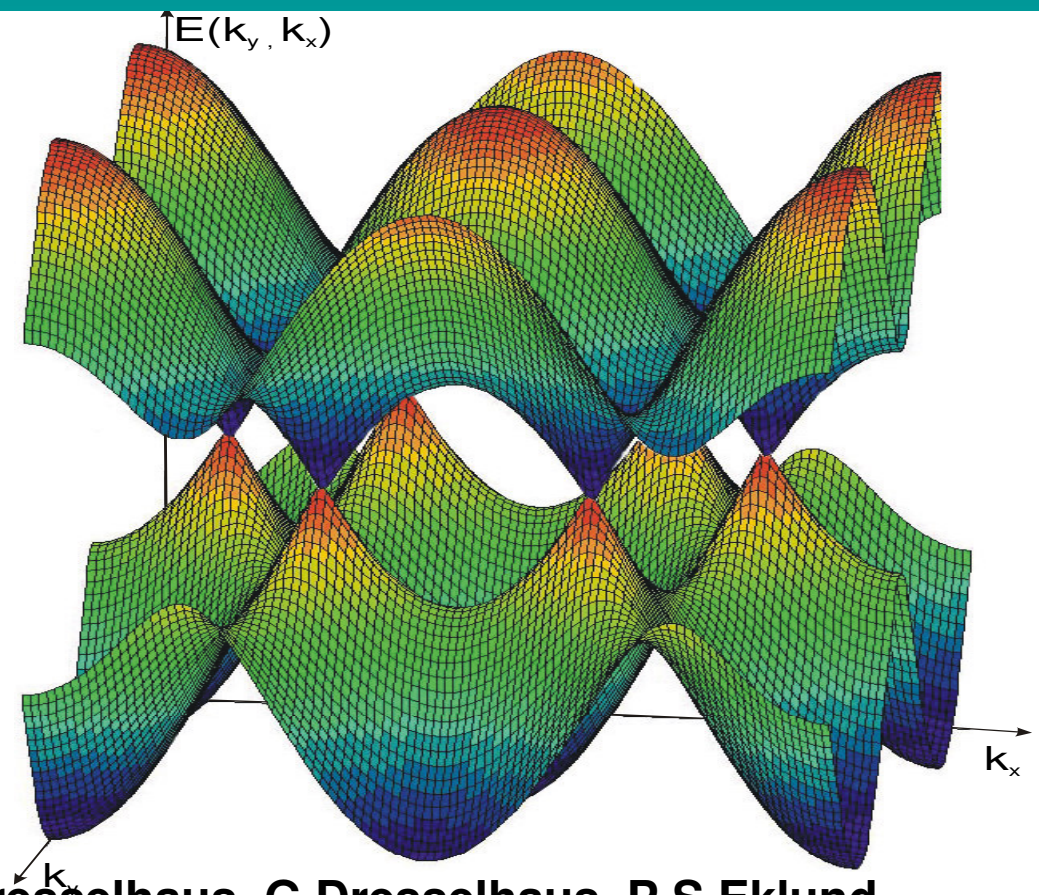




S. Maruyama's site

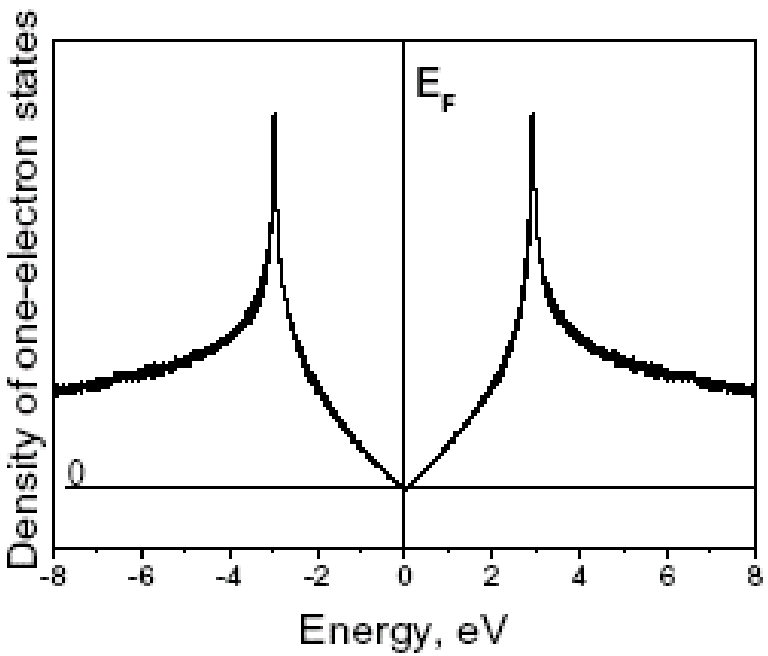
http://www.photon.t.u-tokyo.ac.jp/~maruyama/nanotube.html

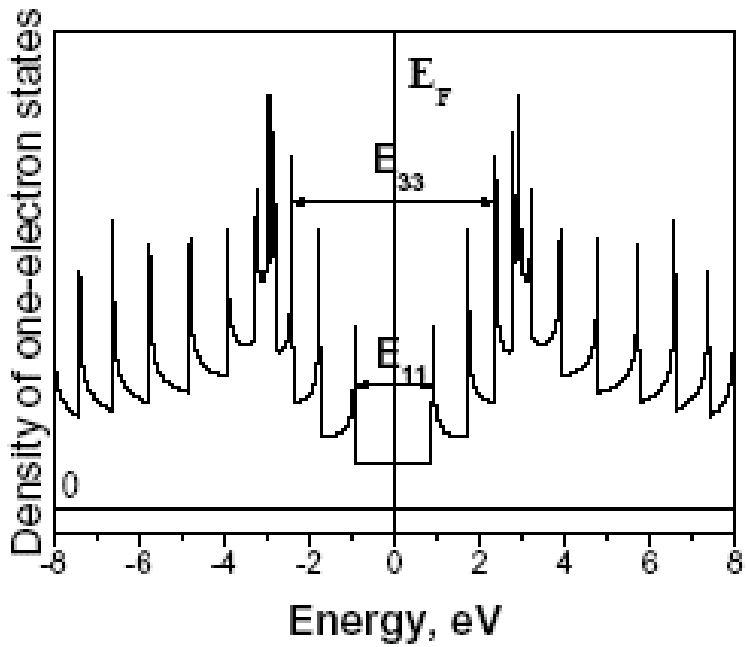
Two-dimensional electron dispersion in graphene

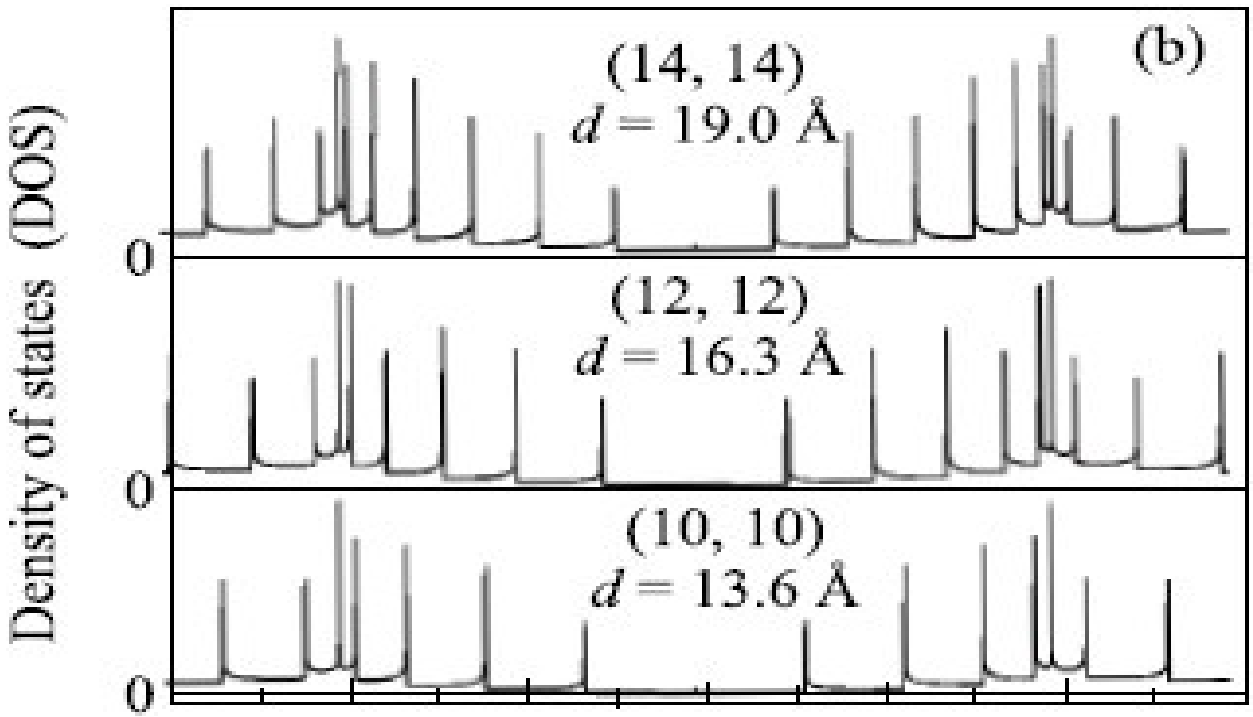


1. .Dresselhaus, G.Dresselhaus, P.S.Eklund, "Science of Fullerenes and Carbon Nanotubes", Academic Press, San Diego, CA, 1996.

Density of one-electron states in graphene and in single-wall carbon nanotube



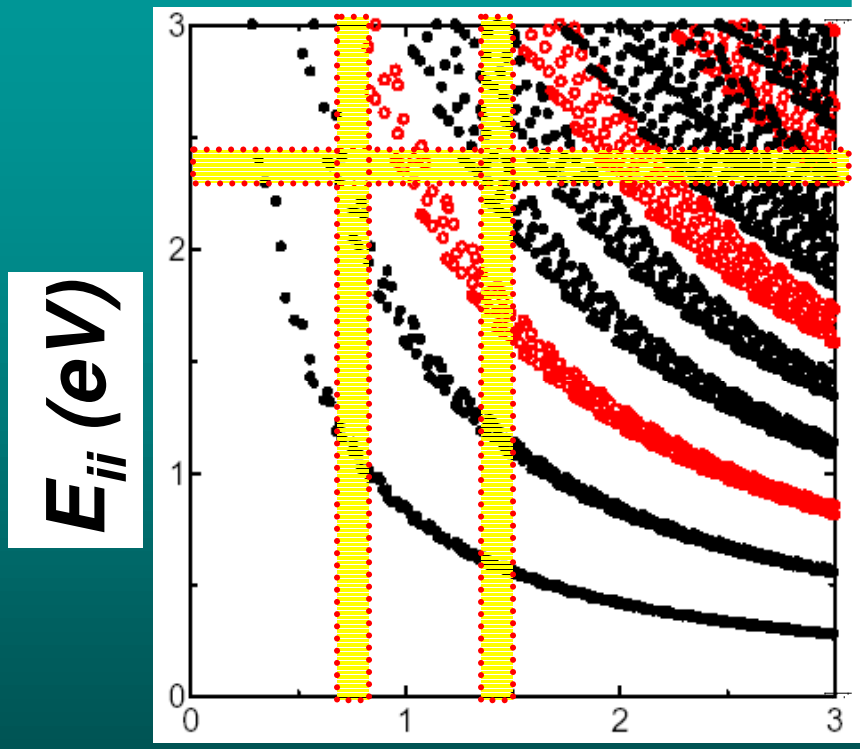


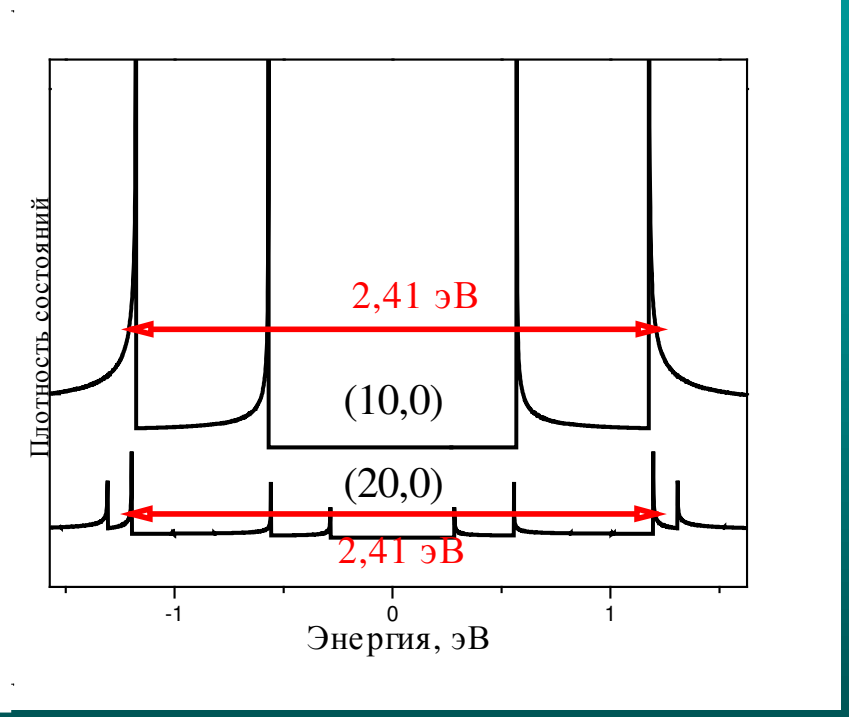


A.V. Osadchy et al., JETP Lett. 77 (2003) 405-410

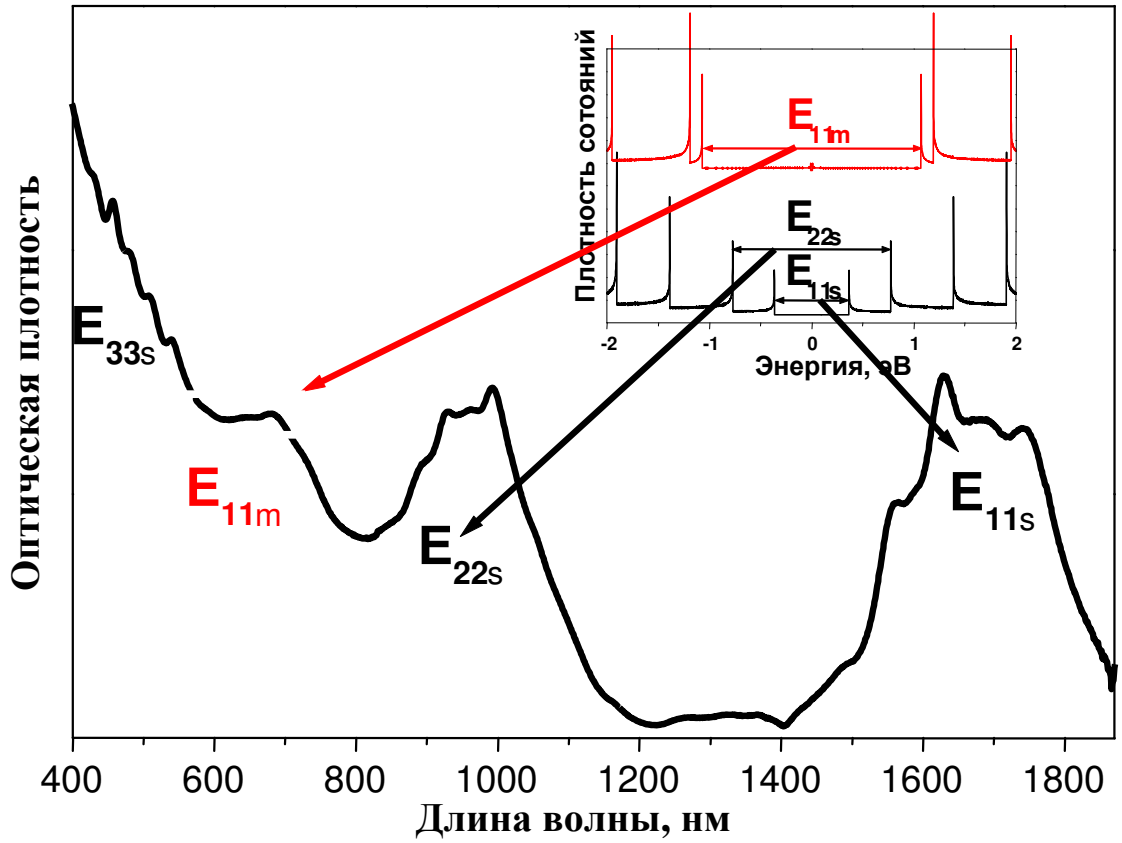
Kataura-plot:

dependence of the electron transition energy on nanotube diameter

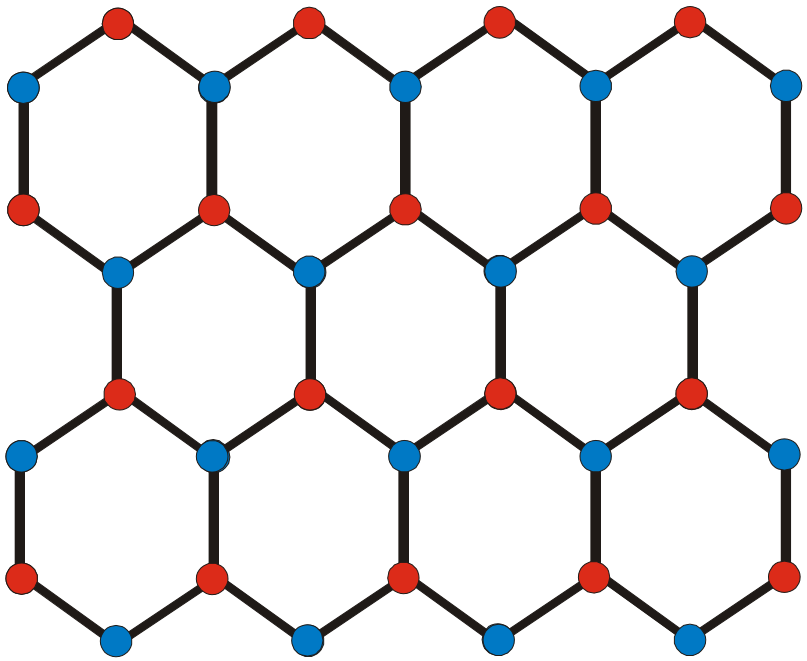




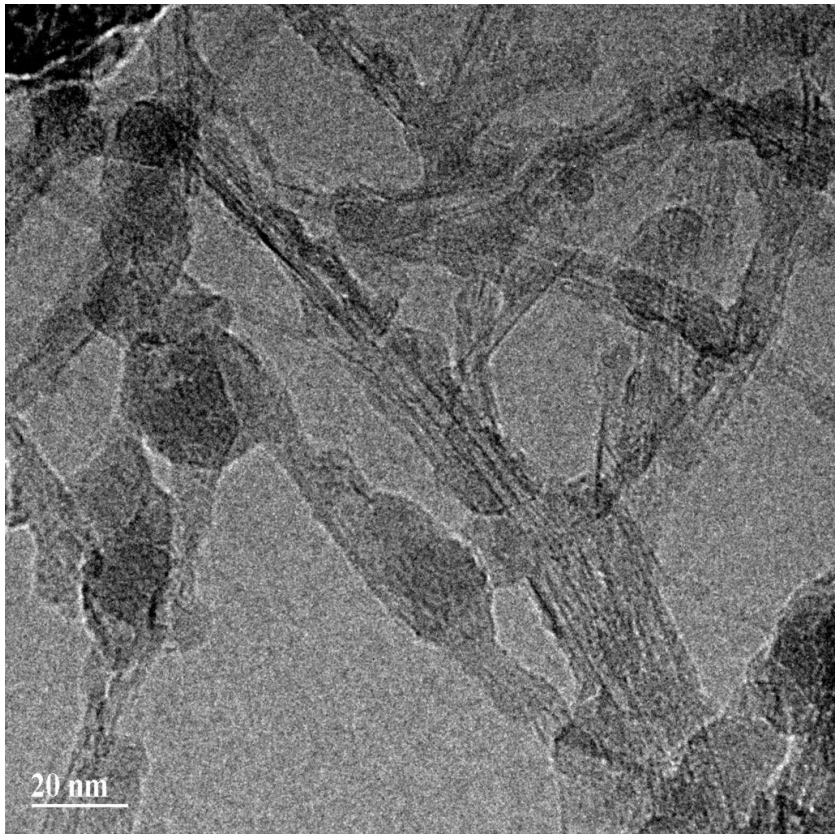
A typical UV-VIS-NIR optical absorption spectrum of single-wall carbon nanotubes



Boron nitride single-wall nanotubes

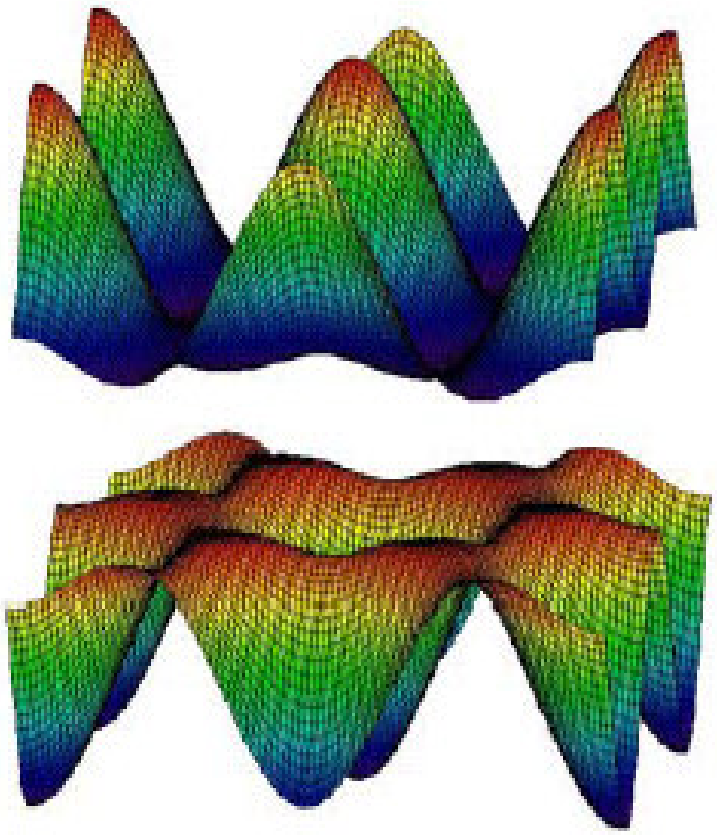


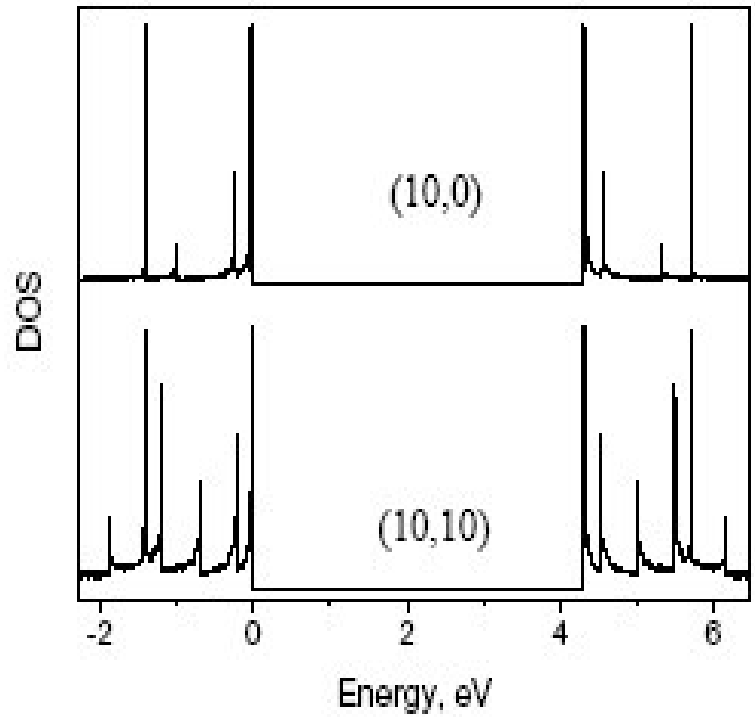
Boron atom **(B)** Nitrogene atom **(N)**



R.S.Lee et al., PRB 64 (2001)121405

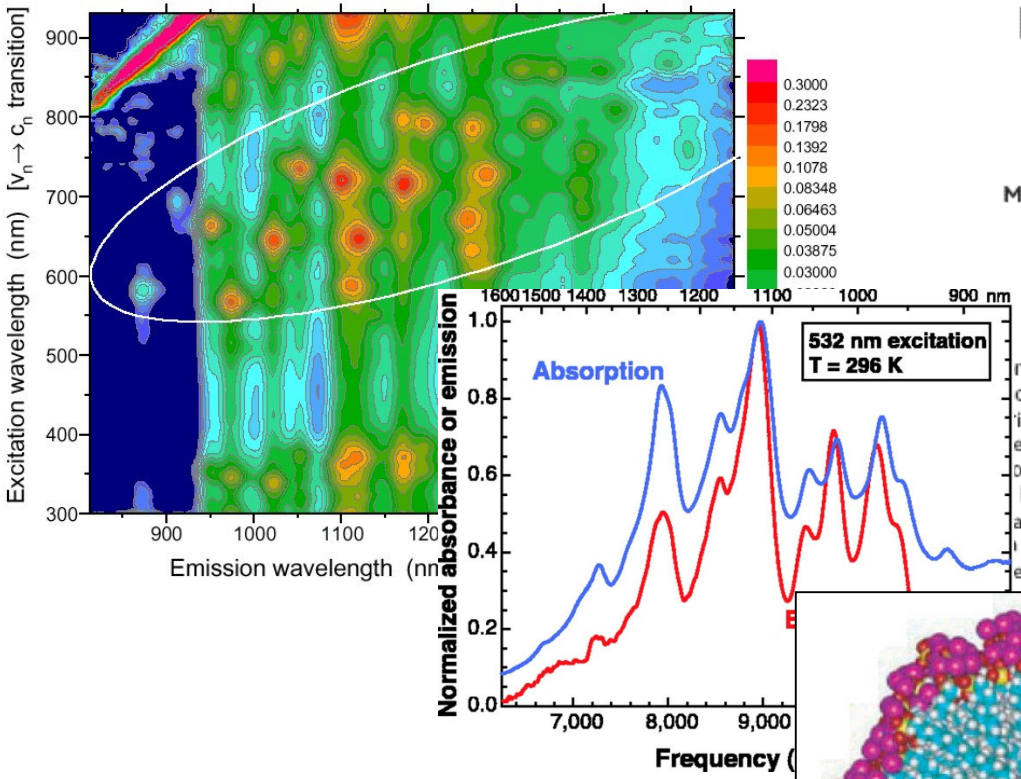
All BN nanotubes are semiconductors





A.V. Osadchy, et al., JETP Letters (2002)

Photoluminescence in single-wall carbon nanotubes?



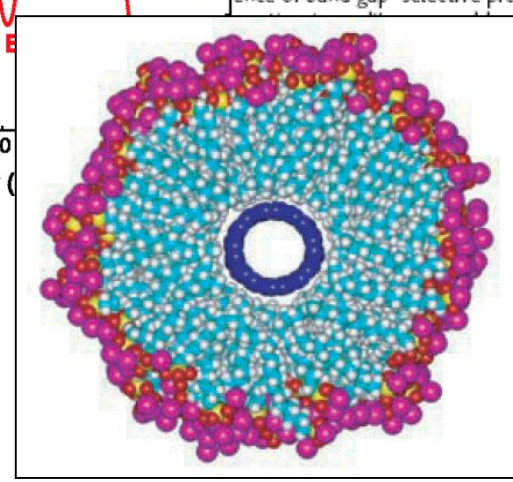
Band Gap Fluorescence from Individual Single-Walled Carbon Nanotubes

Michael J. O'Connell,[1] Sergei M. Bachilo,[1] Chad B. Huffman,[1] Valerie C. Moore,[1] Michael S. Strano,[1] Erik H. Haroz,[2] Kristy L. Rialon,[1] Peter J. Boul,[1] William H. Noon,[3] Carter Kittrell,[1] Jianpeng Ma,[3,4] Robert H. Hauge,[1] R. Bruce Weisman,[1] Richard E. Smalley[1,2]*

rescence has been observed directly across the band gap of semiconducting on nanotubes. We obtained individual nanotubes, each encased in a cy- rical micelle, by ultrasonically agitating an aqueous dispersion of raw single- ed carbon nanotubes in sodium dodecyl sulfate and then centrifuging to ove tube bundles, ropes, and residual catalyst. Aggregation of nanotubes bundles otherwise quenches the fluorescence through interactions with allic tubes and substantially broadens the absorption spectra. At pH less 5, the absorption and emission spectra of individual nanotubes show ence of band gap–selective protonation of the side walls of the tube. This treatment with base or ultraviolet light.

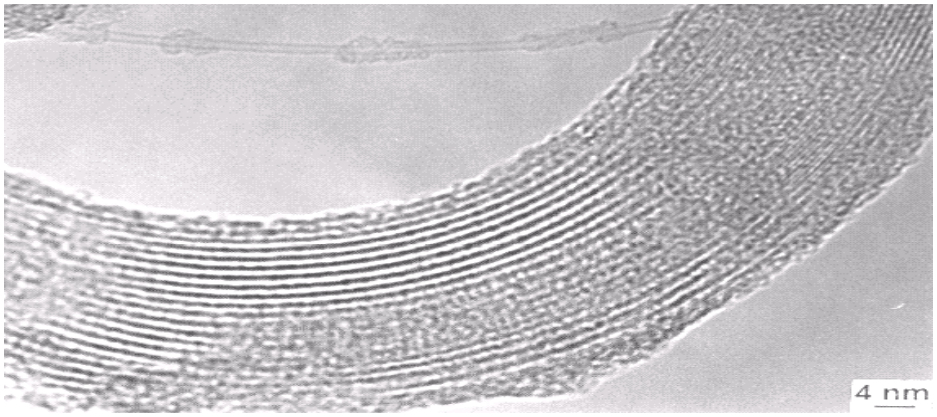
t- polarizable, smooth-sided fullerene t
at readily form parallel bundles or ropes w
i- van der Waals binding energy of ~50
al per micrometer of tube-tube contact (3
ts This bundling perturbs the electronic s
n- ture of the tubes, and it confounds al

26 July 2002



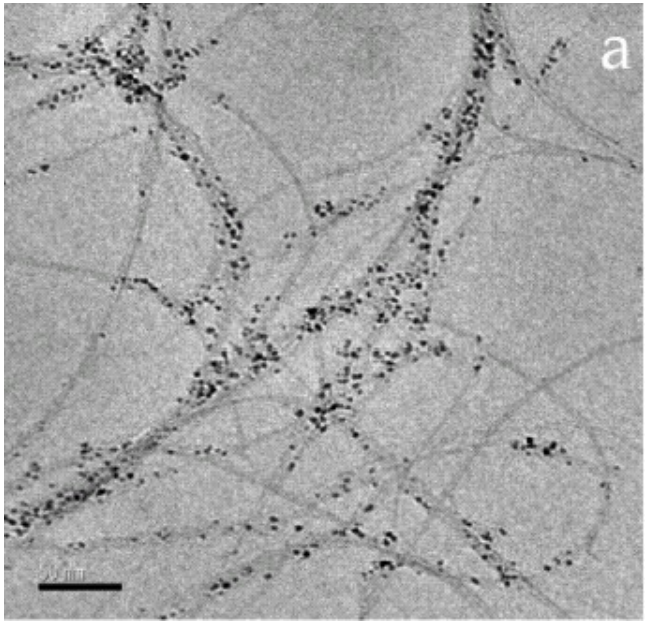
Science ***297,*** *593 (2002)*

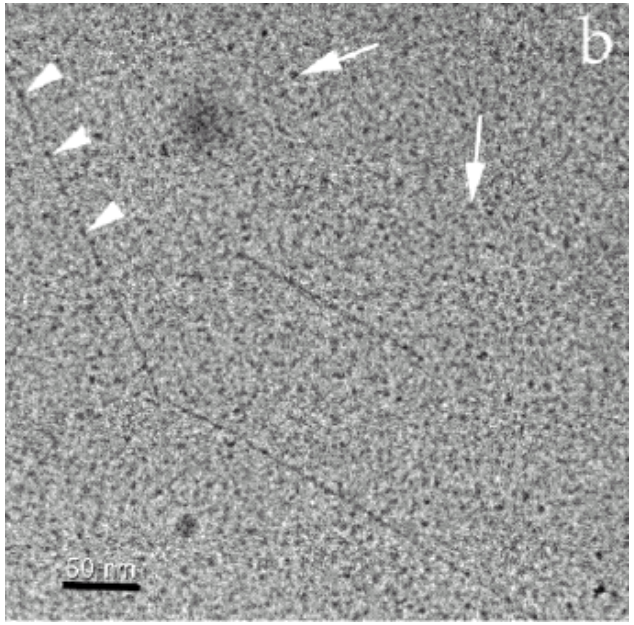
Science ***298,*** *2361 (2002)*



As-grown nanotube bundle

M.Montioux et al., Carbon 39 (2001) 1251

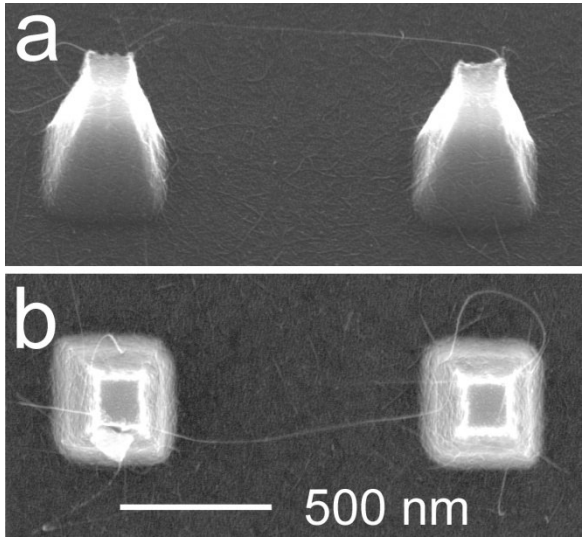




Cryo-HRTEM of suspension

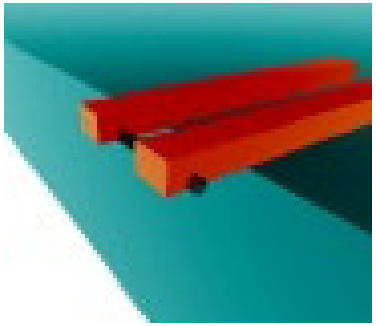
V.C. Moore, M.S. Strano et al., NanoLetters 3(2002)1379

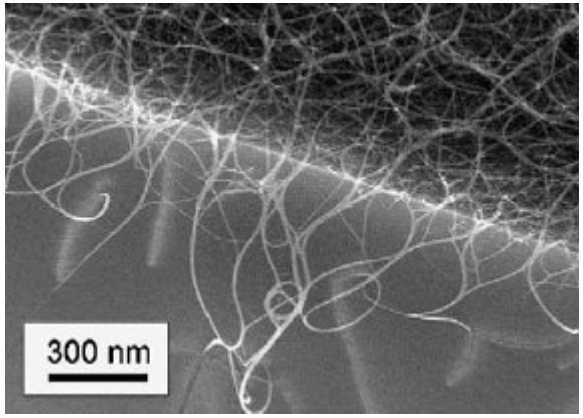
Different ways to get individual nanotubes



J. Lefebvre et al., *PRB 69, 075403 (2004)*

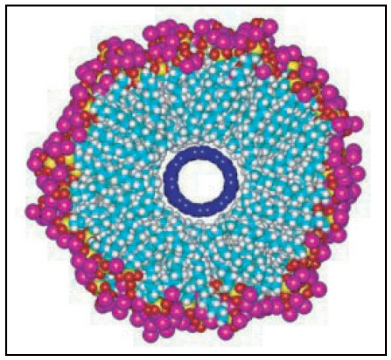
J.Meyer et al.,
cond-mat/0501341-v2-2005

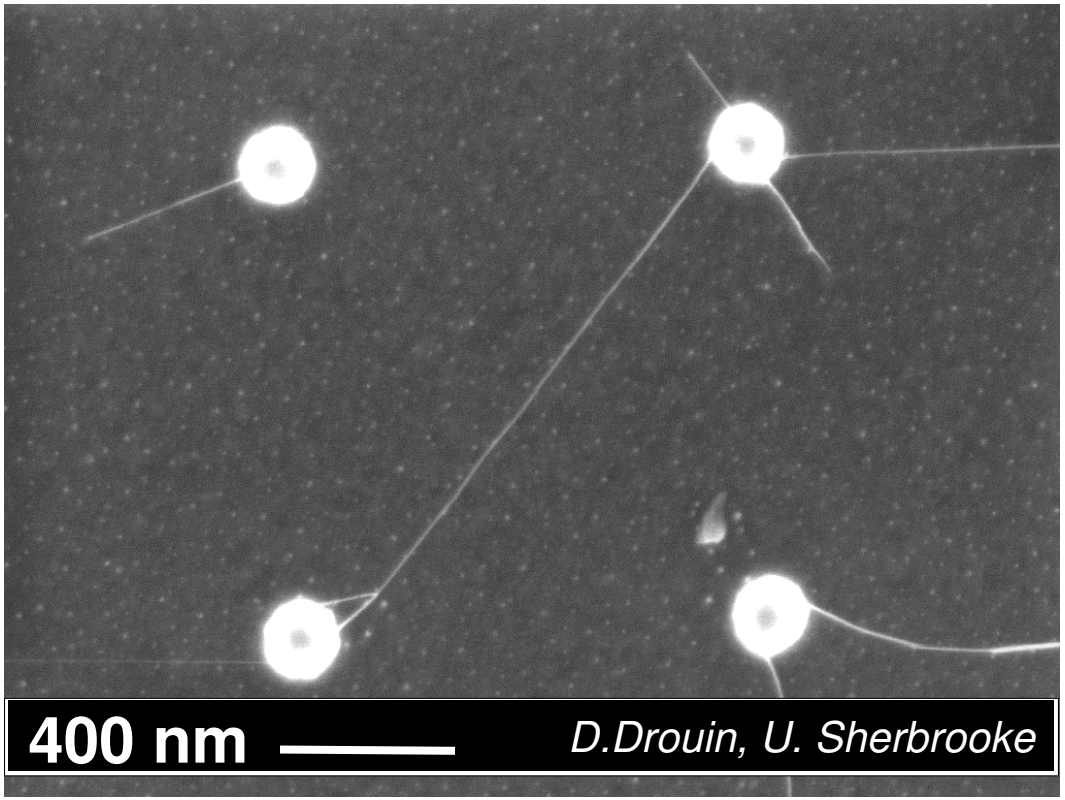




Y. Murakami et al.,
CPL 377(2003)49.

M. O'Connel et al.
Science 297 (2002) 593.

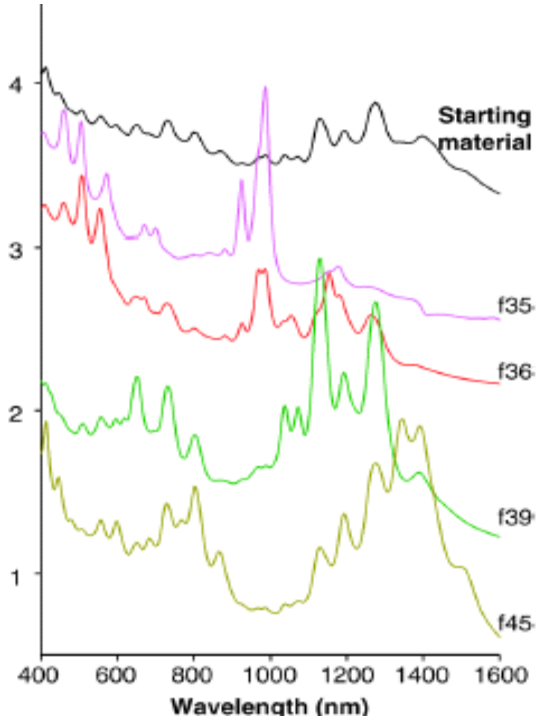


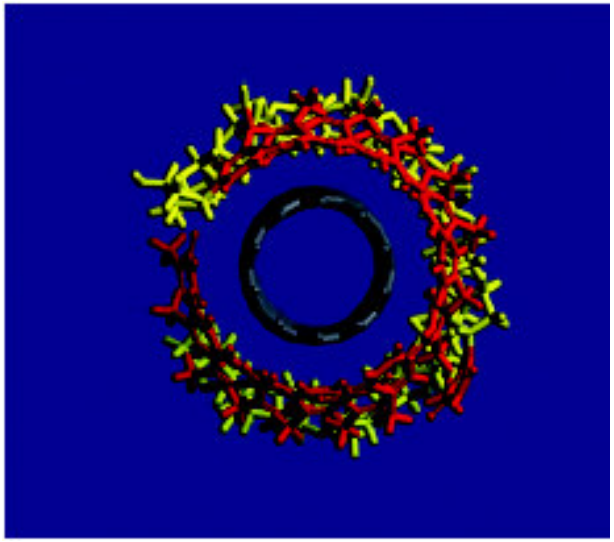


- Si or SiO_2 pillars
- uniform ≈1 nm Fe or Co catalyst
- methane CVD, 800-950 ^{o}C

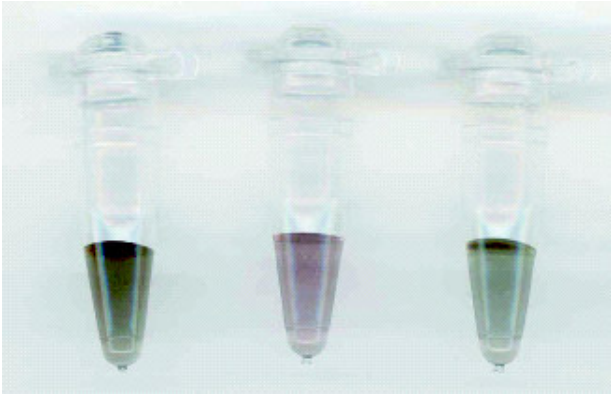
APL ***81,*** *2261 (2002)*

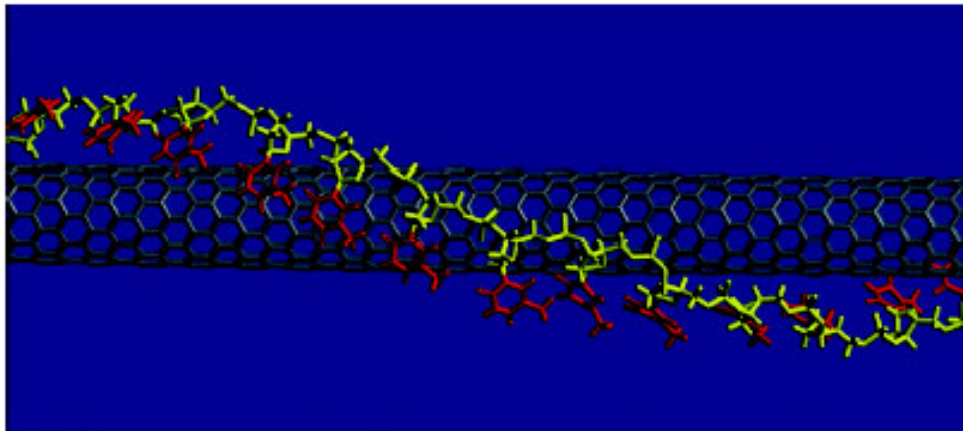
DNA-assisted separation of nanotubes



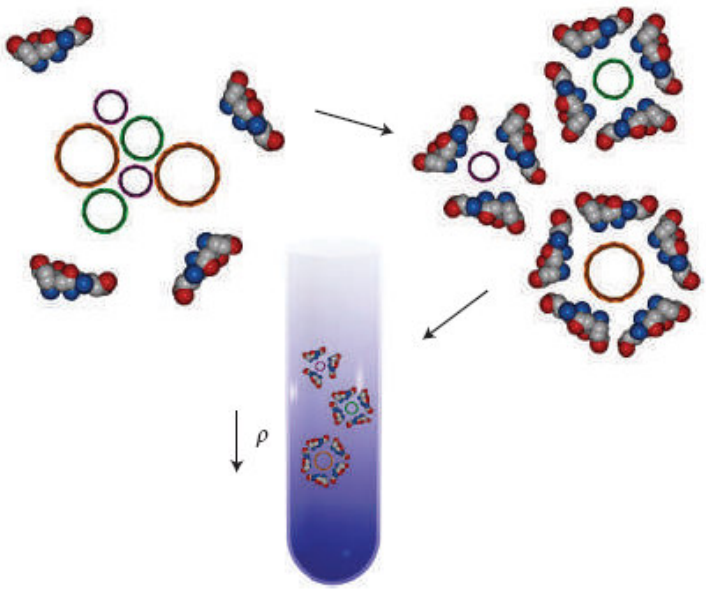


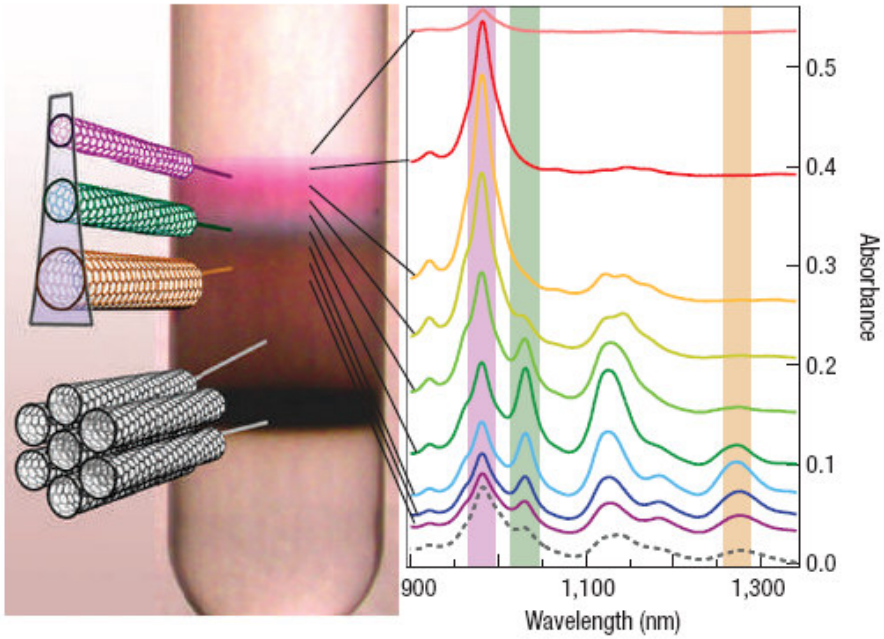
M.Zheng et al., Science 302(2003)1545





Density gradient centrifugation – a way to get nanotube fractions with a narrow diameter distribution

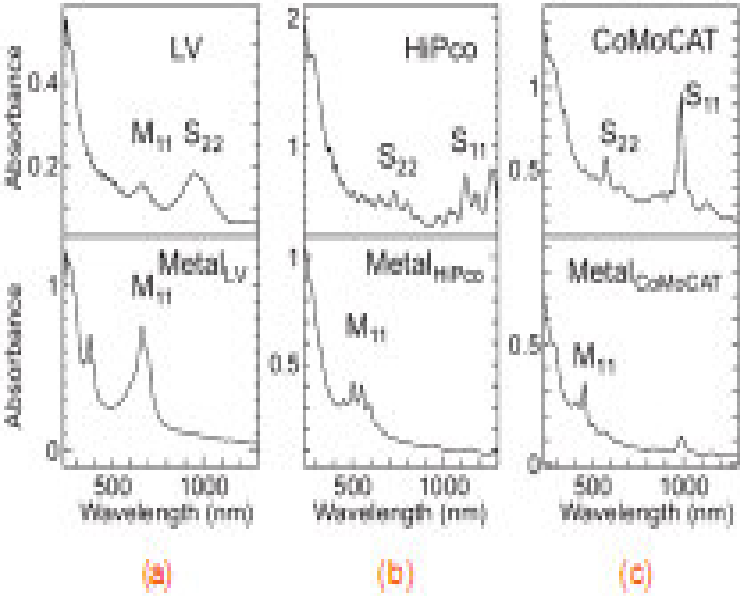




Iodixanol

M.S. Arnold, A.A. Green, J.F. Hulvat, S.I. Stupp and M.C.Hersam, Nature Nanotechnology 1 (2007) 60.

Separation of metallic and semiconducting nanotubes



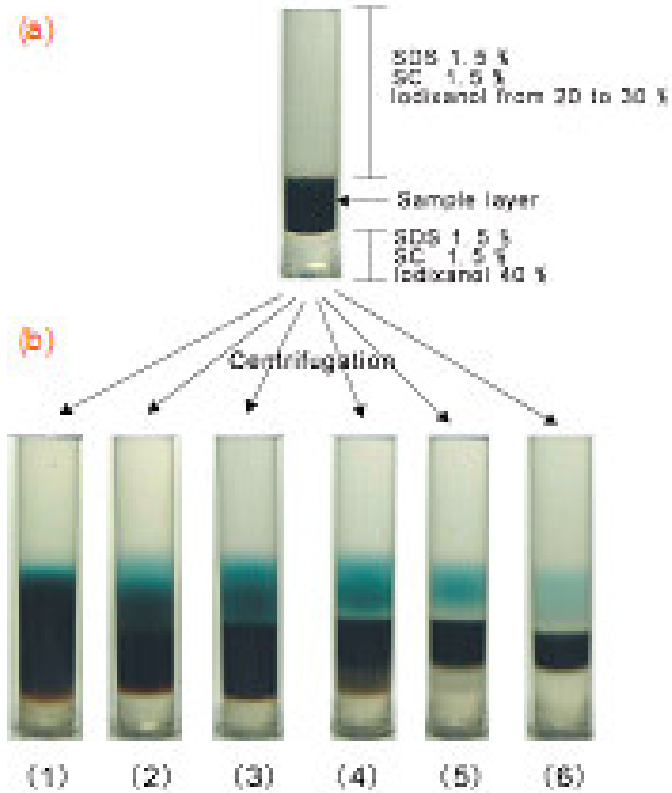
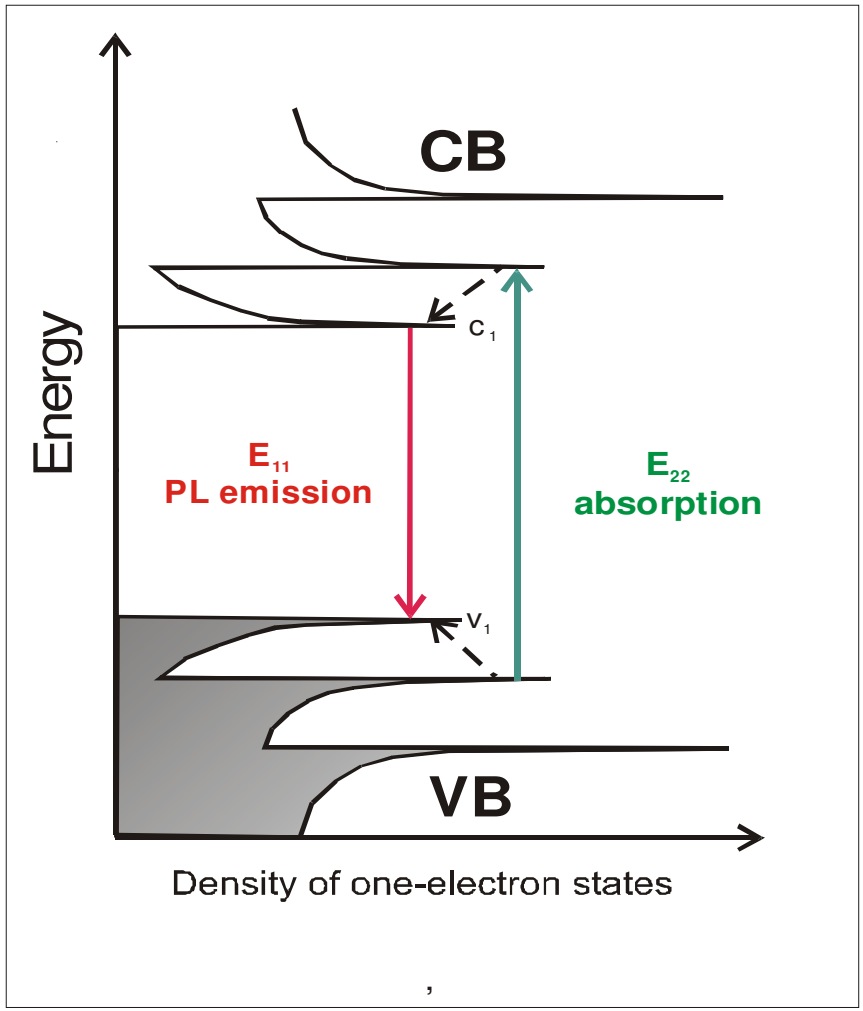
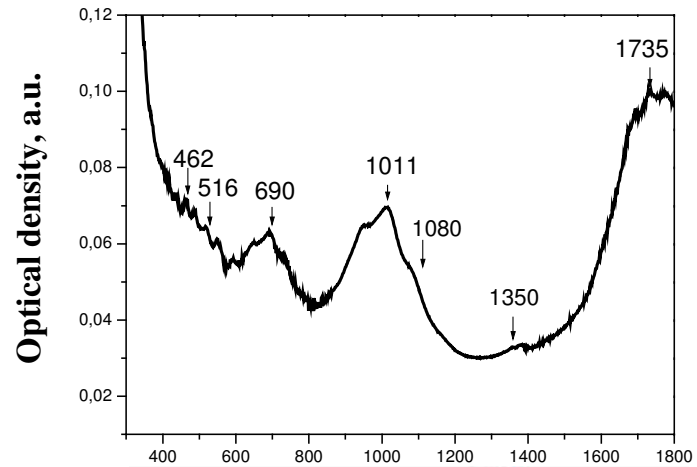


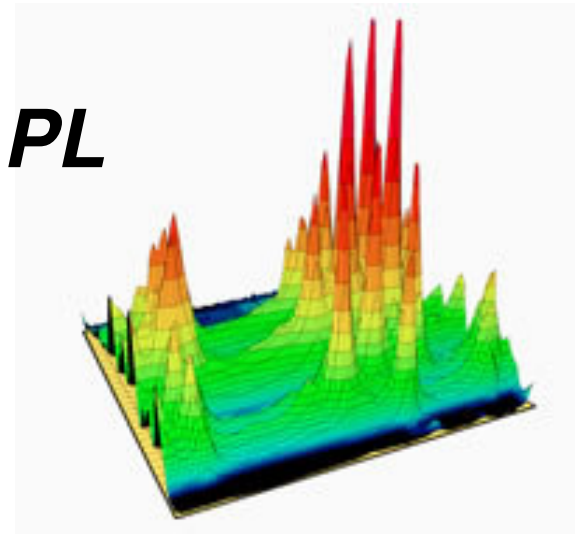
Fig. 1. Pictures of centrifuge tubes (a) before and (b) after centrifugations in LV nanotubes. The concentration of iodixanol in a sample layer was 30%. The concentrations of surfactants in the centrifuge tube (except the sample layer) were set to be SDS 1.5%, SC 1.5%. Those concentrations in the sample layer were (1) SDS 1.5%, SC 1.5%, (2) DOC 0.25%, SDS 1.5%, SC 1.5%, (3) DOC 0.5%, SDS 1.5%, SC 1.5%, (4) DOC 0.5%, SDS 1.0%, SC 1.0%, (5) DOC 0.5%, SDS 0.5%, SC 0.5%, and (6) DOC 0.5%.

K.Yanagi, Y. Miyata, and H. Kataura,
Appl. Phys. Express 1(2008) 034003

Electronic transitions in nanotubes



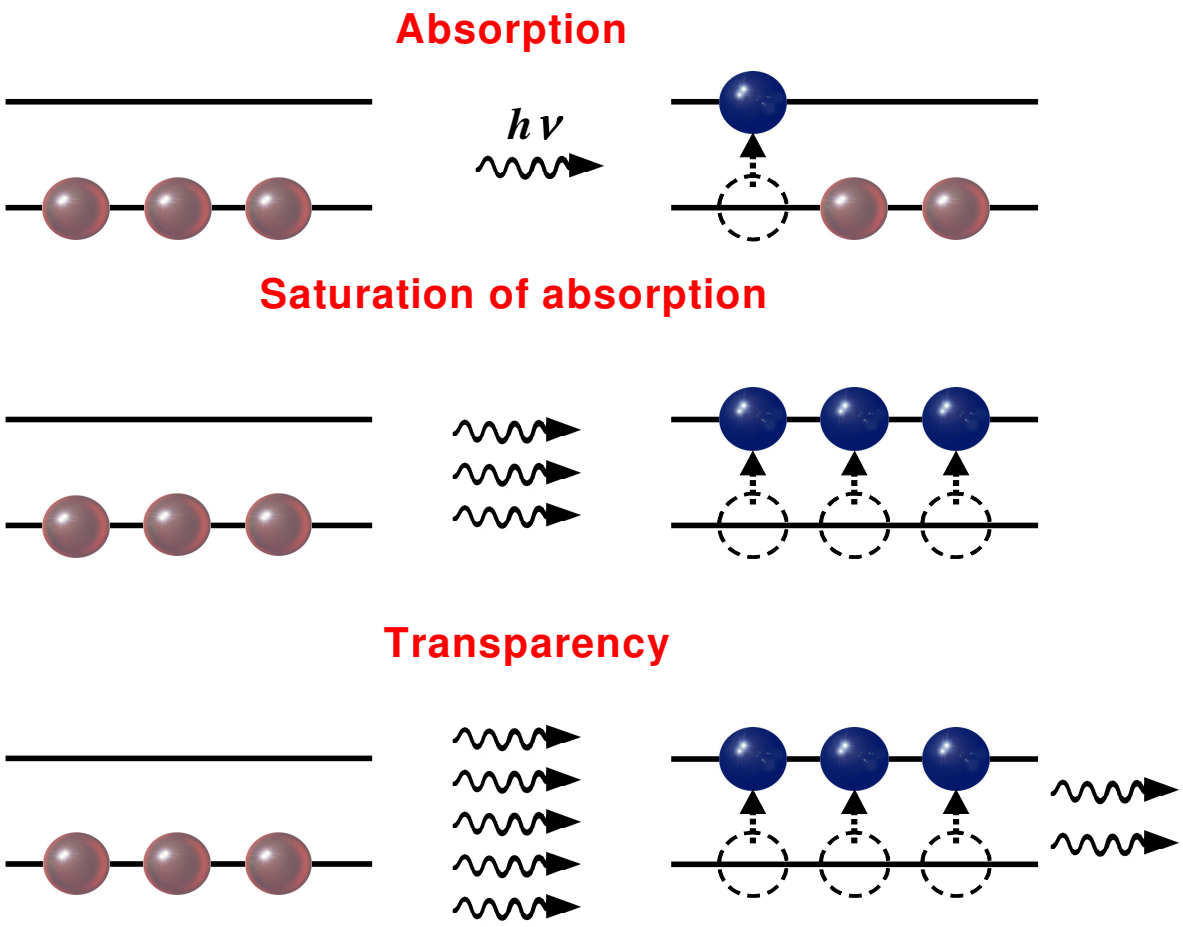




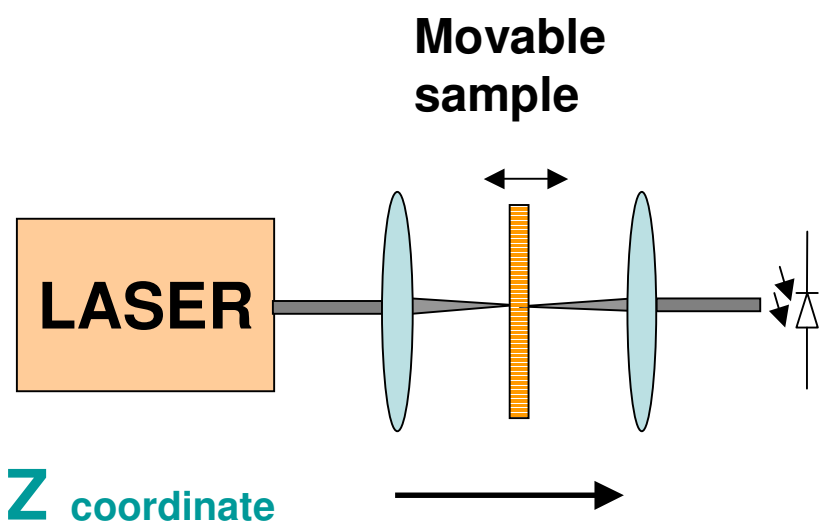
Weisman et al.

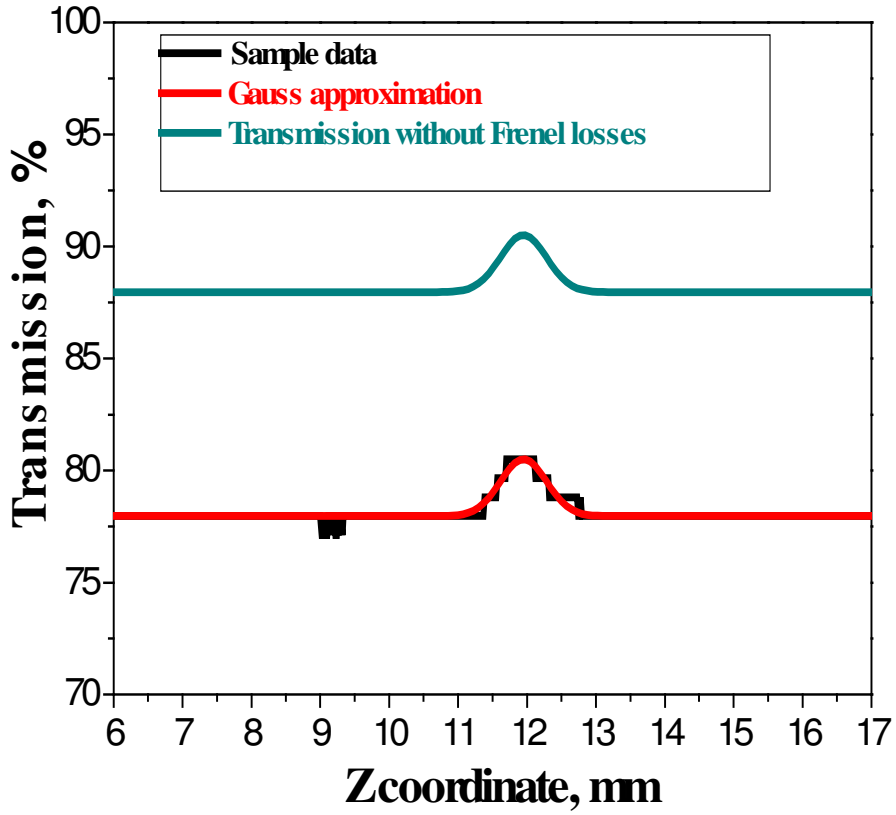
Non-linear optical properties of carbon nanotubes

Laser-induced transparency (saturable absorption)



Z-scan measurements of saturable absorption



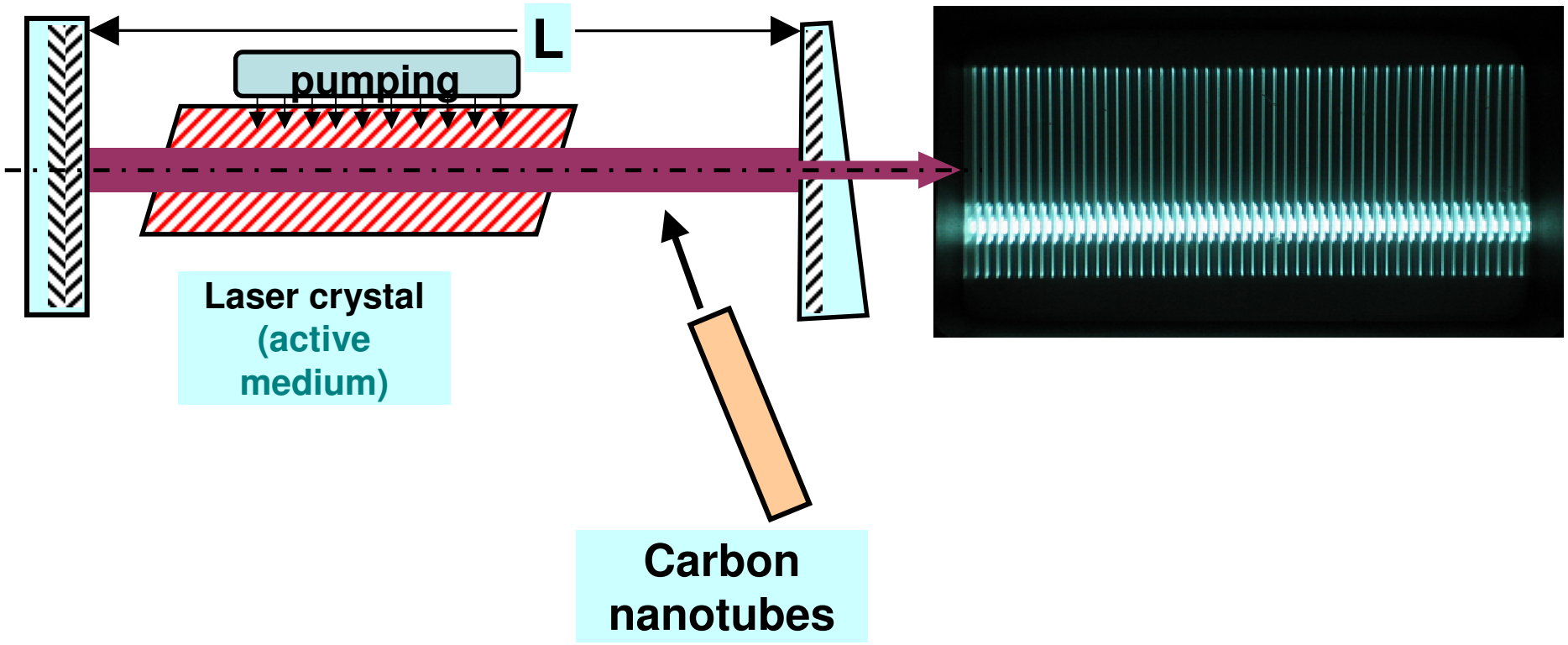


Passive mode locking

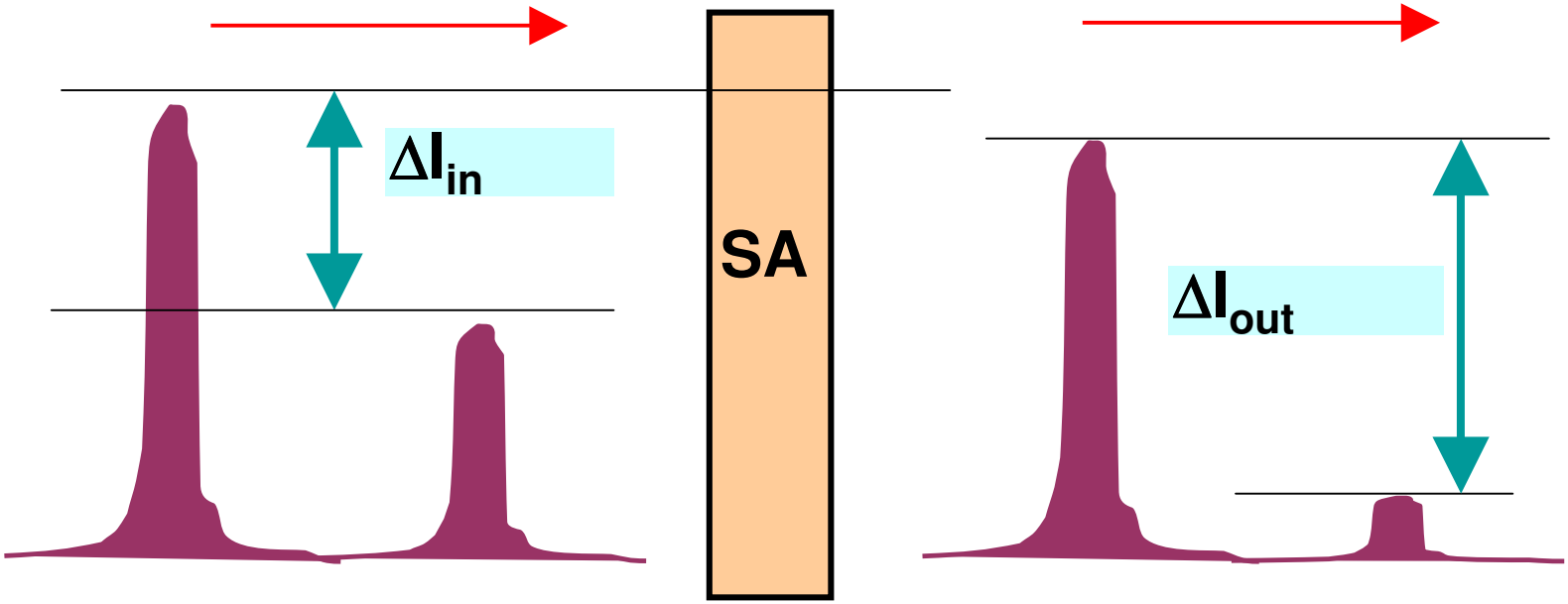
continious *wave* laser radiation →

train of femtosecond pulses

Output radiation



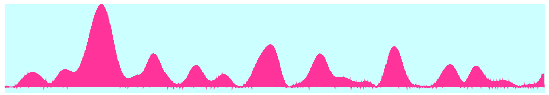
Discrimination of the laser pulses of different intensity with a saturable absorber



Self mode-locking:

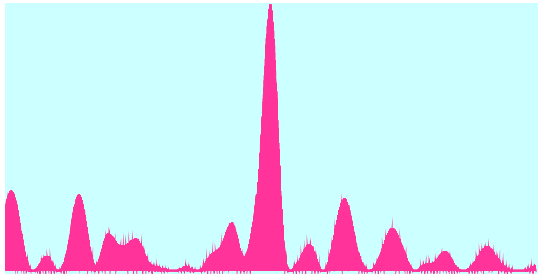
regularization of the laser output and generation of ultrashort pulses

Laser output without saturable absorber t_0

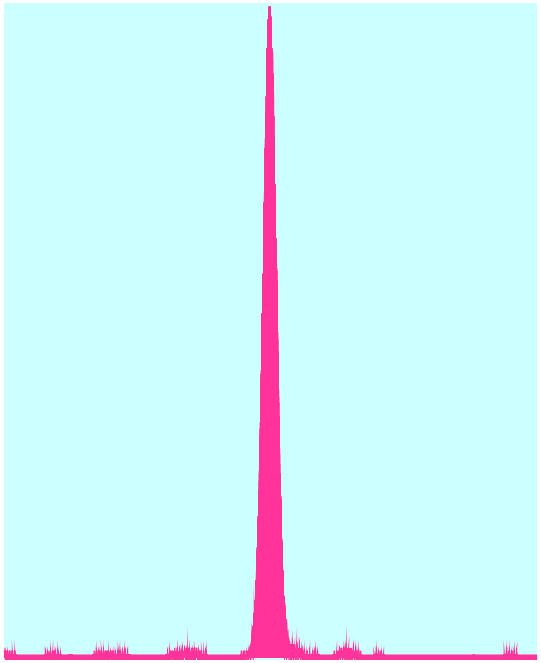


with saturable absorber

t_1 ~10 x 2L/c ►

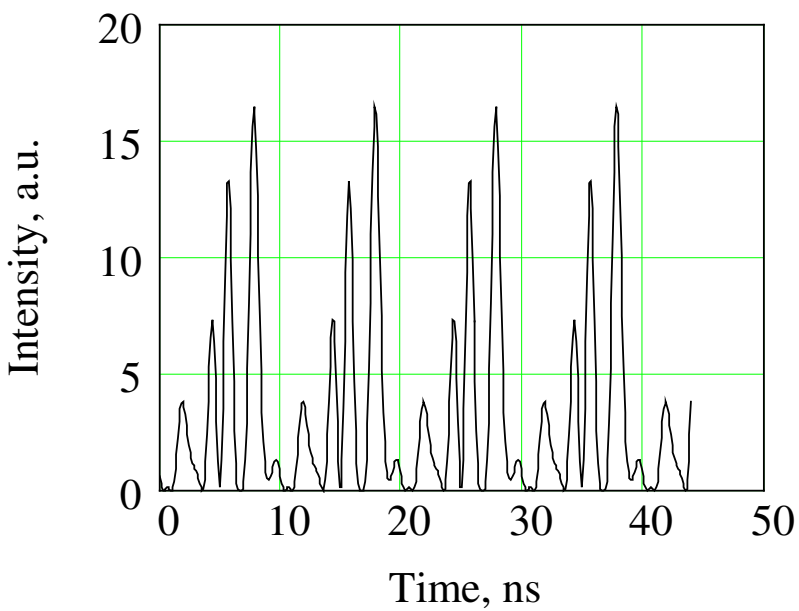


t_2 ~100 x 2L/c ►



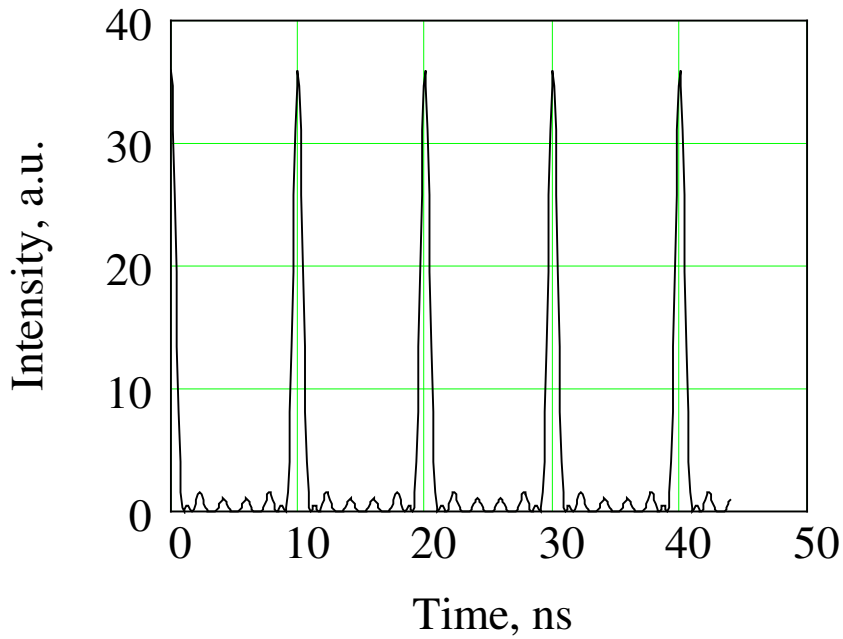
Random phases

(simulation, number of modes 6)



Mode locking

(simulation, number of modes 6)



Where do we need femtosecond pulses?

For optical communications:

to increase the information density in optical communications in the range of 2 “transparency windows” of optical fibers – 1.53-1.58 μm and 1.29-1.34 μm.

For medical application:

To create reliable and simple lasers for ophthalmology and laser surgery
with the pulse duration of 800-900 fs – to avoid the thermal damage of surrounding tissue.

For spectroscopy:

To perform the optical spectroscopy with a high temporal resolution.

MATERIALS USED for PASSIVE MODE LOCKING

- **Organic dyes**
- **Color centers in crystals (LiF:F_2^-, alkali halides:*F*, …)**
- **Semiconductor quantum dots**
- **Metallic nanoparticles (Ag, Au) embedded in glass matrix**
- **«SESAM» :**
  non-linear mirror (multilayer Fabry-Perot resonator)
  Keller U., *Nature 424 (2003) 831.*

Single-wall carbon nanotubes (SWNTs) possess
a combination of unique properties

guarantying their efficiency in

ultrafast optical switching in different solid states lasers:

- a wide working spectral range (1-2 mkm),
- an ultrafast relaxation of electronic excitations (with sub-picosecond characteristic times),
- a high optical non-linearity,
- a high resistivity against laser damage,
- a low threshold for the regime of ultrafast laser pulse generation.

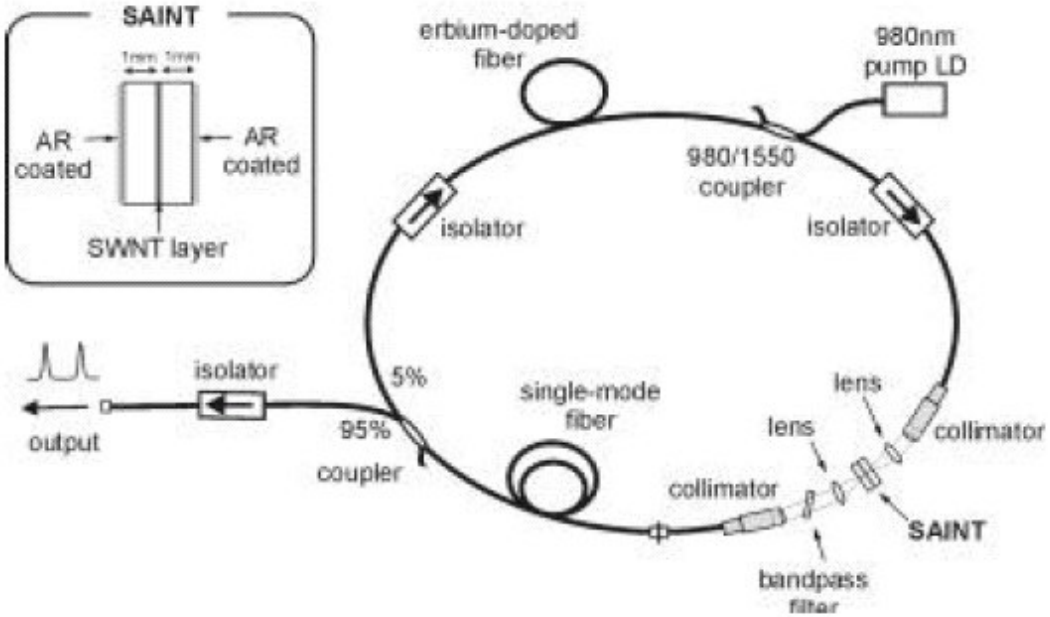
Recent achievements in demonstration of the mode locking regime with single-wall carbon nanotubes.

1. ***Demonstration of a principal possibility to get mode locking with carbon nanotubes.***

2. ***Different lasers and saturable absorbers based on carbon nanotubes***

A first mention
about using *the SWNTs as a saturable absorber*

S.Y.Set, H.Yaguchi, Y. Tanaka, M. Jablonski et al. **"Mode-locked Fiber Lasers based on a Saturable Absorber Incorporating Carbon Nanotubes"**, ***Book of Abstracts of OFC'03,USA, # PDP44, 2003.***



SAINT- Saturable Absorber Incorporating NanoTubes

Progress in development of *SWNT-based saturable absorbers*

2003 - **SWNT film spayed onto the quartz slab** *(S.Y. Set et al.)*

2004 – **Liquid suspensions of individual SWNTs** *(Il'ichev et al., Quantum electronics 34 (2004) 572)*

2005 – **polymer films incorporating SWNTs for fiber lasers (***Rozhin et al., CPL 405 (2005) 288.*

2005 – **mirror covered by polymer film with SWNTs for Er3+- solid state laser with bulk elements** *(T.Shibli et al. Optics Express 13 (2005) 8025)*

2006 - **SWNTs in waveguide laser** *(DellaValle et al., APL 89 (2006)231115)*

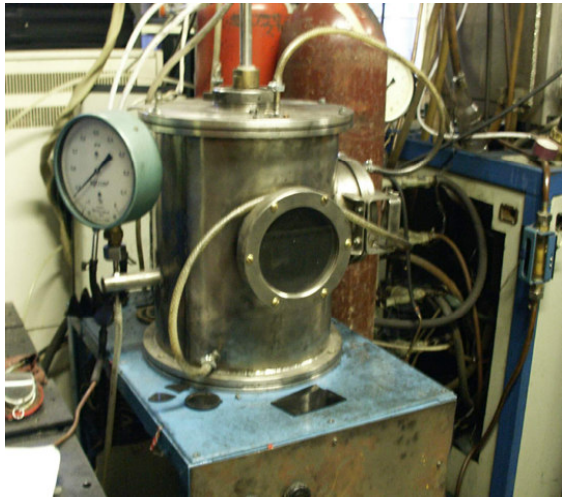
2007 – **cellulose films incorporating SWNTs (for different solid state lasers)**

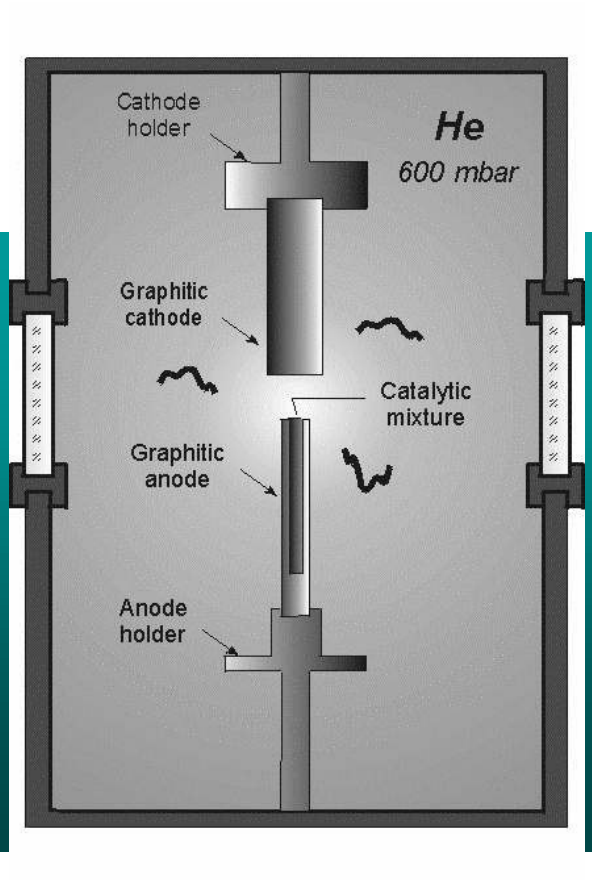
(Tausenev et al., Quantum Electronics 37 (2007) 205)

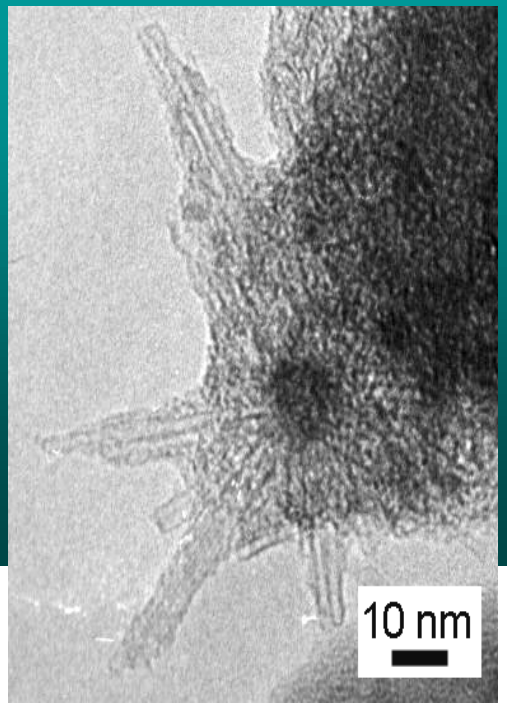
2007 - **SWNTs + SESAM** *(Fong et al., Optics Express 32 (2007) 38)*

Mode locking in Er^{3+}-doped glass solid state lasers

Synthesis of single-wall carbon nanotubes by the <u>electric arc technique</u>

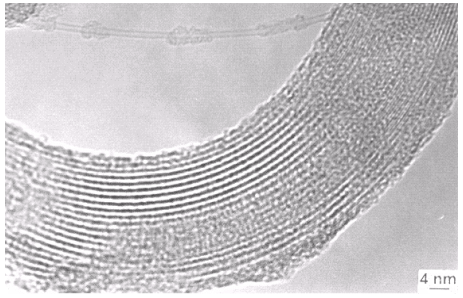


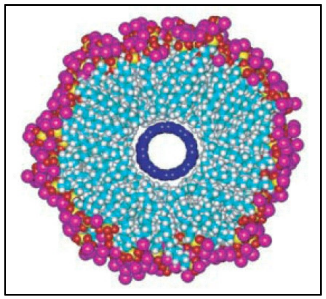


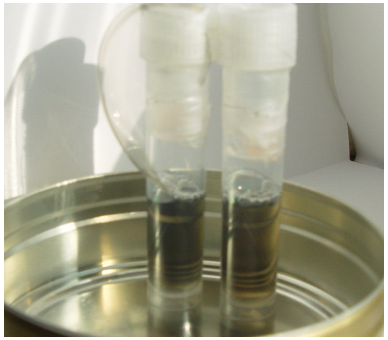


E.D. Obraztsova, J.-M. Bonard, V.L. Kuznetsov et al., Nanostructured Materials 12 (1999) 567.

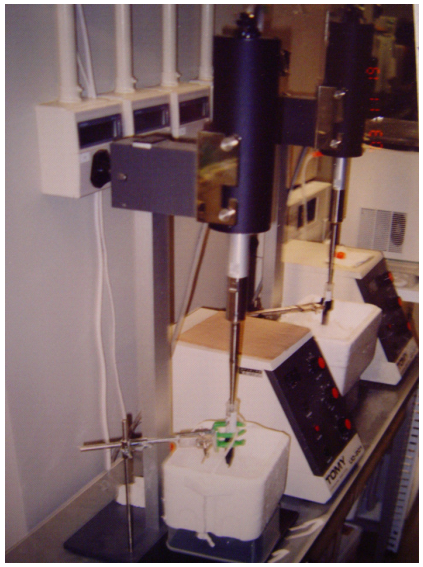
Aqueous suspensions of single-wall carbon nanotubes of optical quality







Method ***(SDBS, DOC)***
Science ***297,*** *593 (2002)*
Science ***298,*** *2361 (2002)*

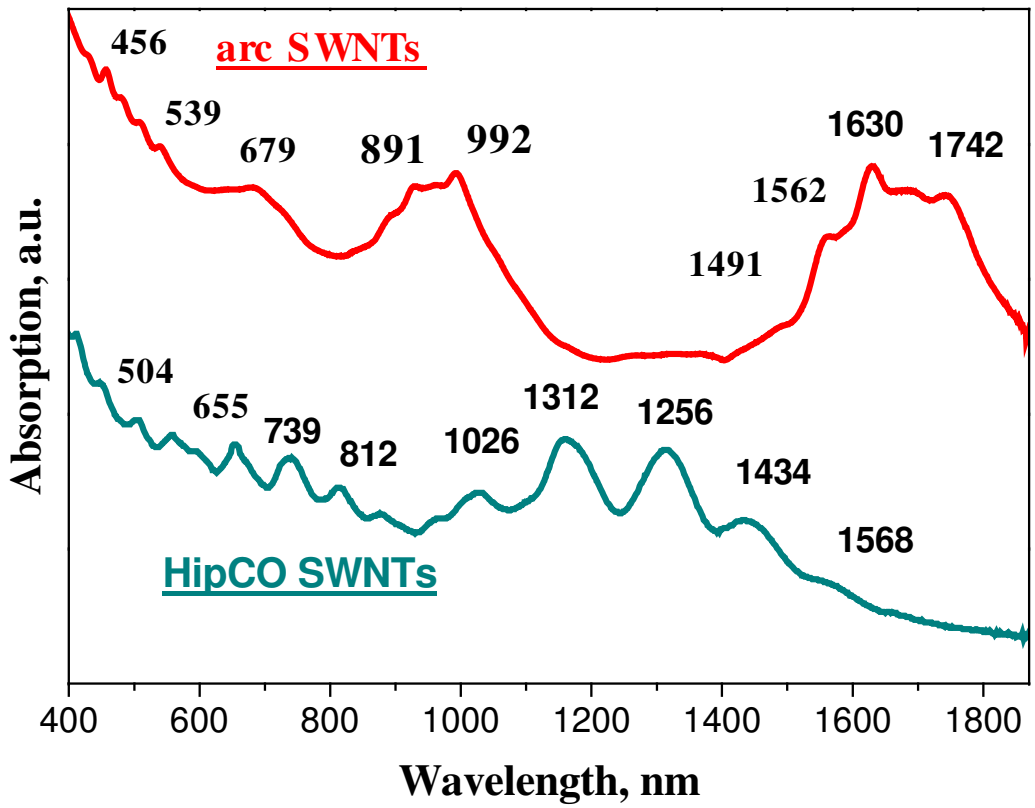


Ultracentrifuging

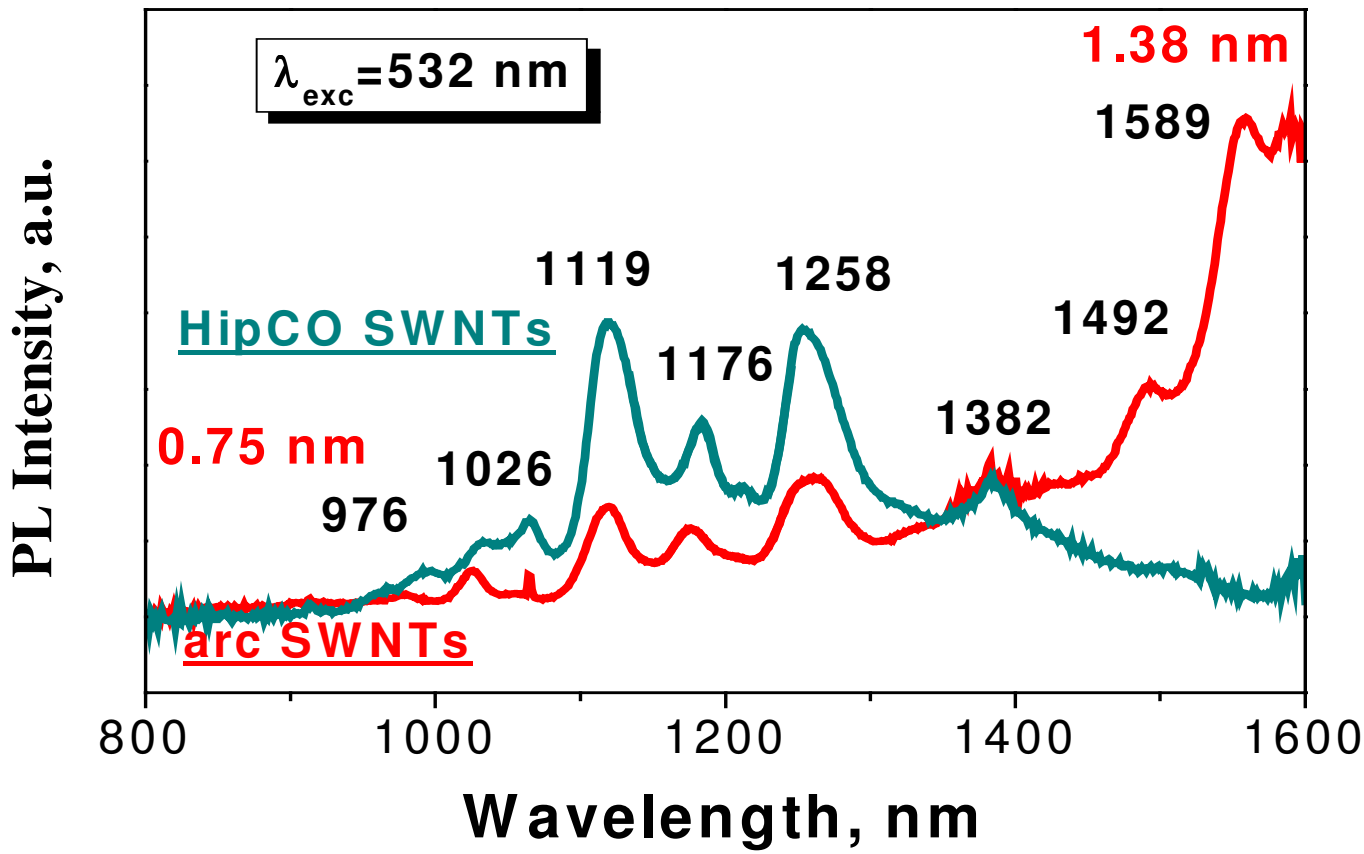
(acceleration >
100 000 g)

Powerful ultrasonication

UV-VIS-NIR optical absorption of aqueous suspensions of single-wall carbon nanotubes

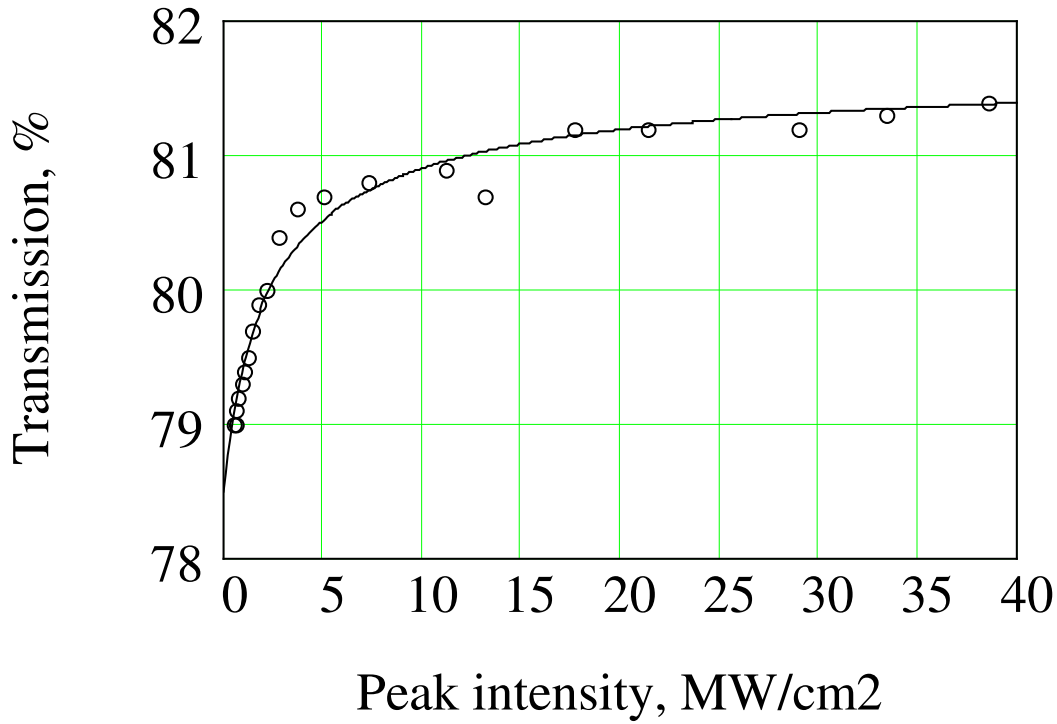


Photoluminescence of aqueous suspensions of single-wall carbon nanotubes



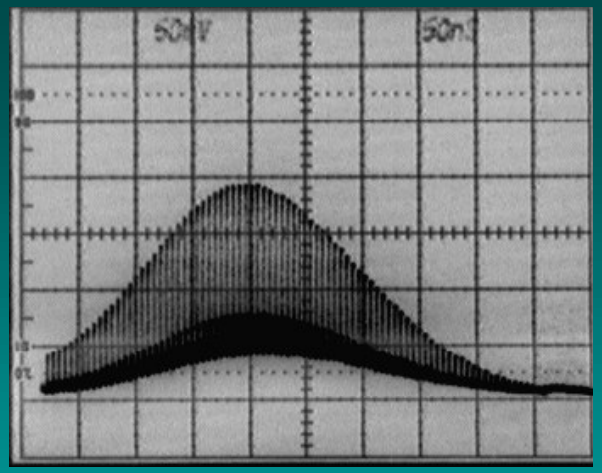
E.D. Obraztsova et al.,"*in the book "Nanoengineered Nanofibrous Materials", NATO Science Series II, Kluwer , v. 169, 2004, p. 389-398.*

Non-linear transmission (λ=1.54 μm) of HipCO single-wall carbon nanotubes in aqueous suspension of SDBS/D_2O



N.N. Il'ichev, E.D. Obraztsova, S.V. Garnov, S.E. Mosaleva , *Quantum electronics 34 (2004) 572*

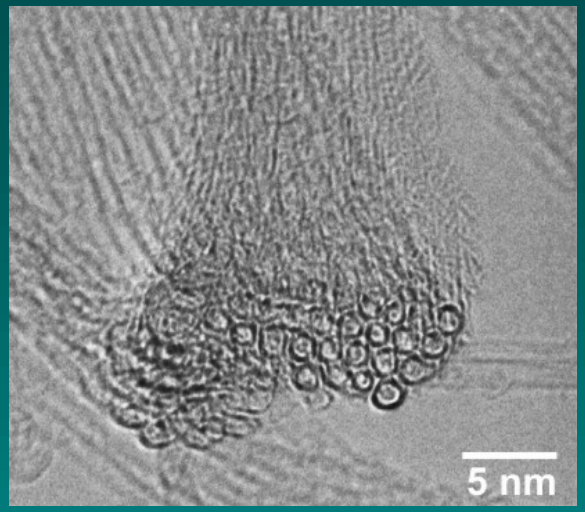
Mode locking in Er^{3+}-glass laser (λ=1.54 μm)

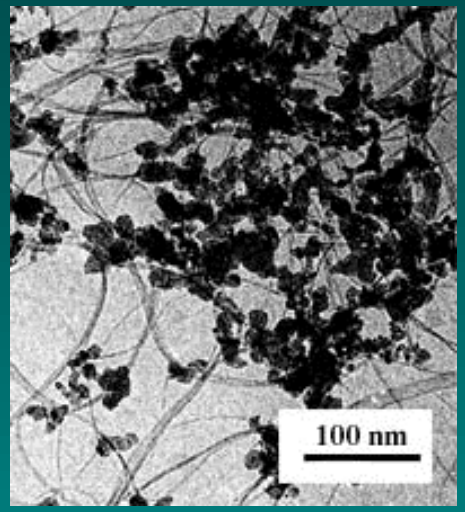


Pulse duration about 20 ps

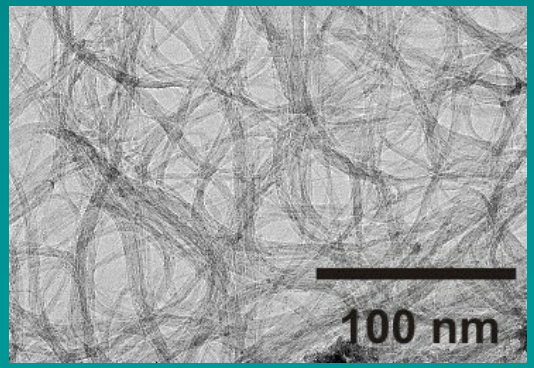
N.N. Il'ichev, E.D. Obraztsova, S.V. Garnov, S.E. Mosaleva , *Quantum electronics 34 (2004) 572.*

A pristine nanotube soot



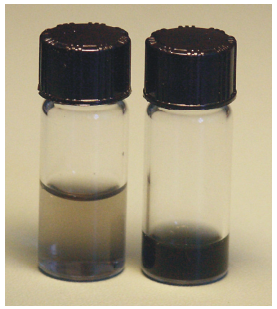


Chemically purified nanotubes



OPTICAL MEDIA

based on single-wall carbon nanotubes

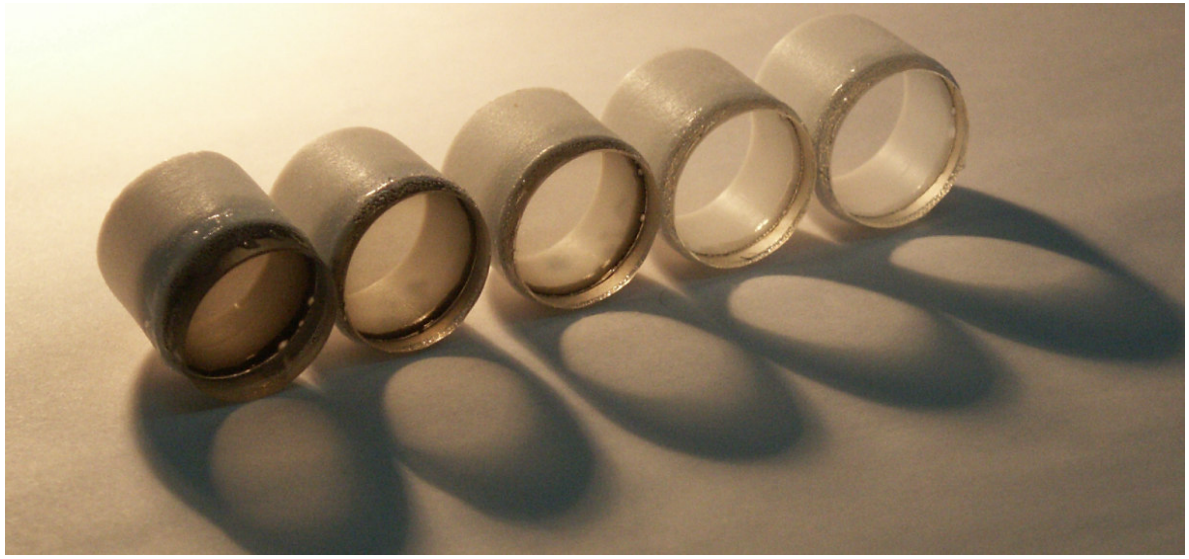


Aqueous suspensions

Polymer films

Optical elements (mirrors, filters)

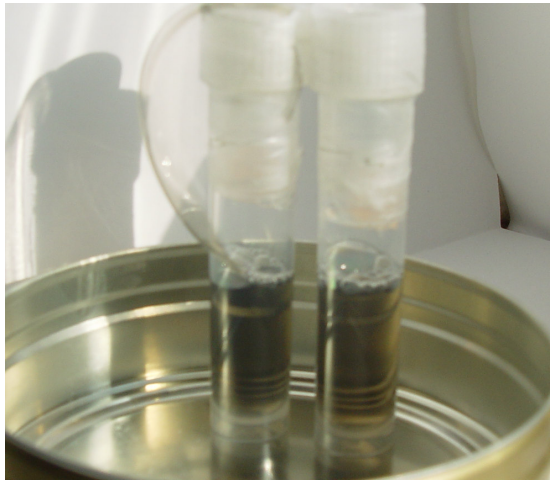
Polymer films incorporating single-wall carbon nanotubes



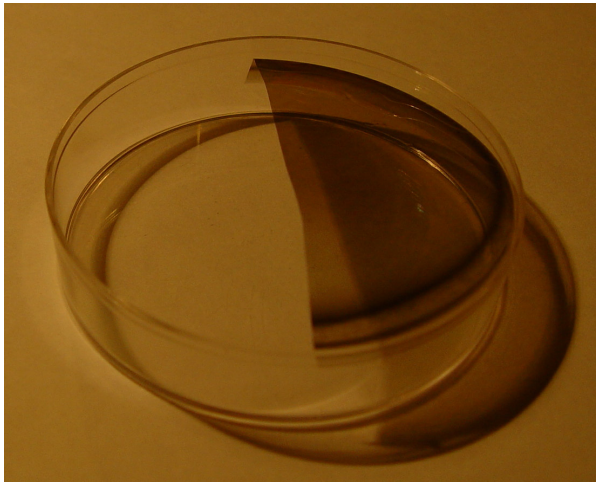
Formation of SWNT-containing polymer films

PvA

or **+** **<u>SWNTs</u>**



=



cellulose

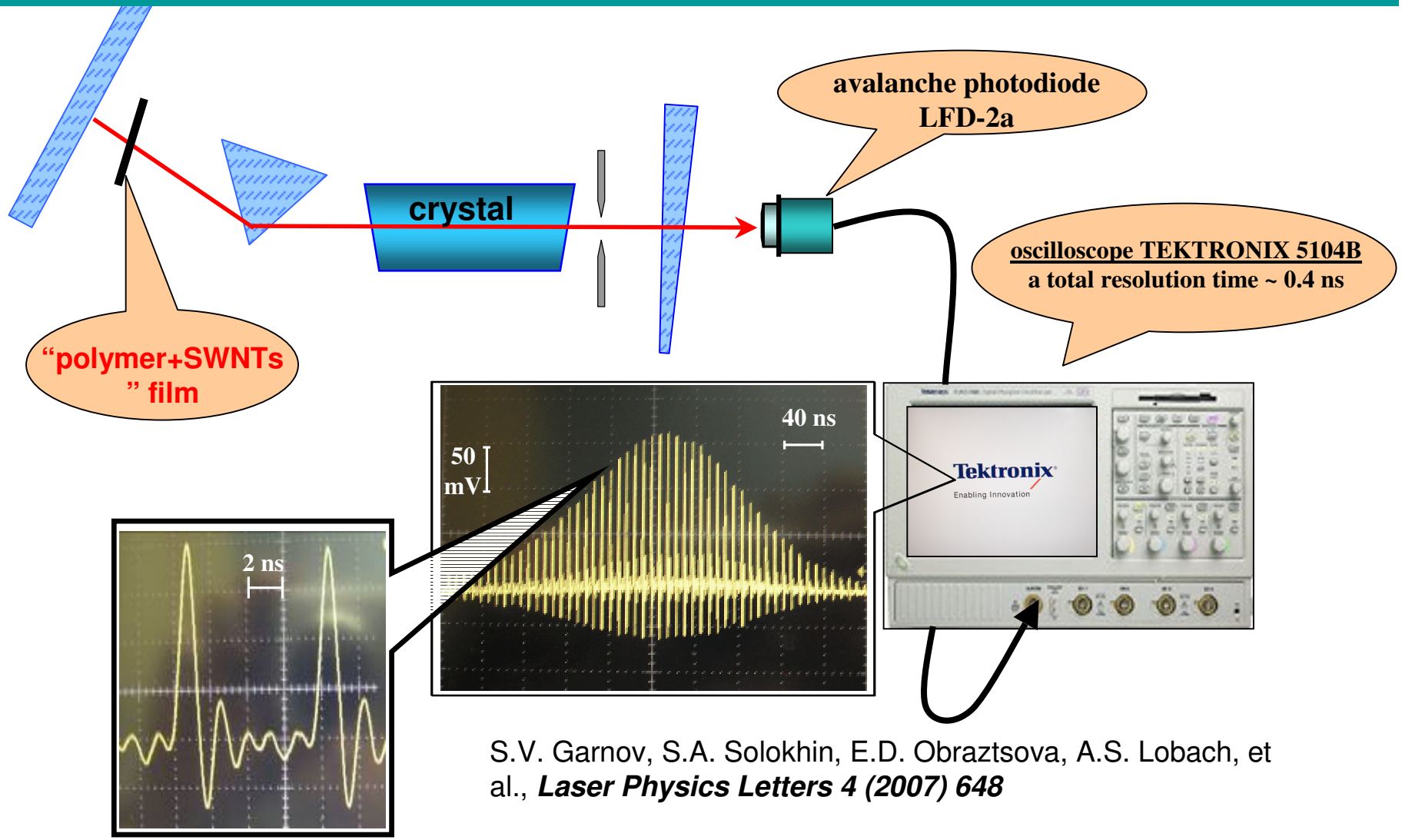
Liquid cast on a smooth substrate followed by a slow drying

Film thickness – 4-50 mkm

A.I. Chernov, E.D. Obraztsova, A.S. Lobach,
Physica Status Solidi (b), 244 (11) (2007) 4231-4235.

Minami N., Kim Y. et al., Appl.Phys. Lett., 88, 093123 (2006).

A temporal profile of the output laser radiation

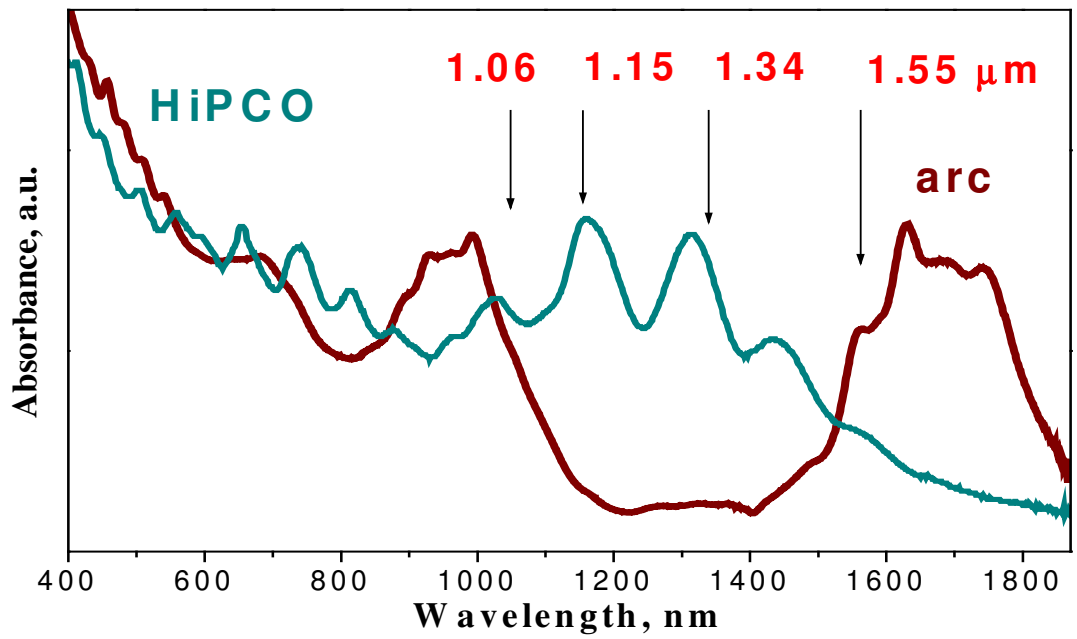


S.V. Garnov, S.A. Solokhin, E.D. Obraztsova, A.S. Lobach, et al., ***Laser Physics Letters 4 (2007) 648***

Operational spectral range of different solid state lasers,

working in mode-lock regime with liquid and film-like

SWNT-based saturable absorbers



S.V. Garnov et al.,
Laser Physics Letters 4 (2007) 648

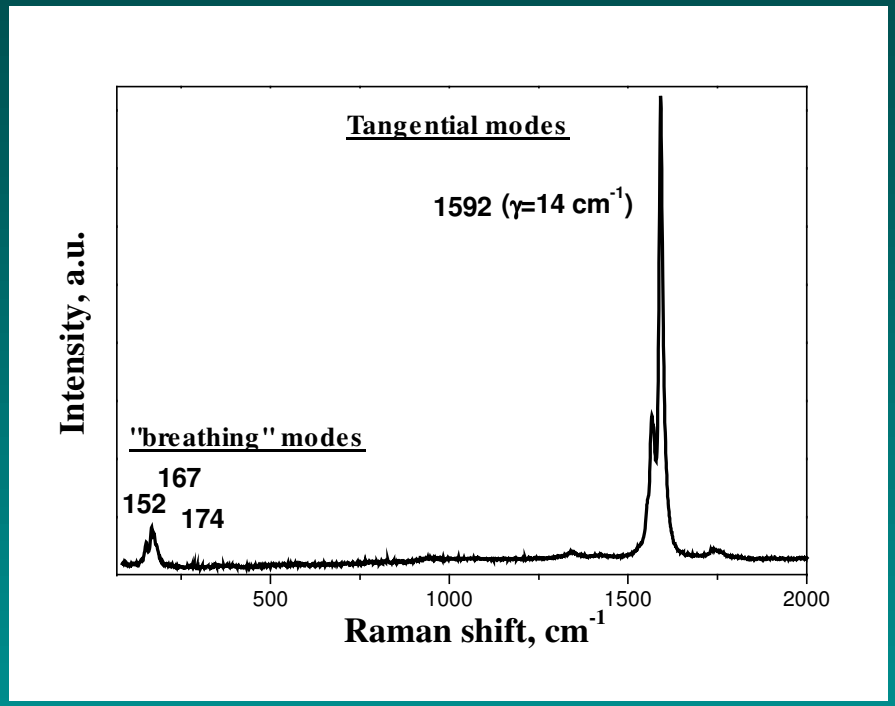
Il'ichev et al., AIP Conf. Proc. 786(2005)611

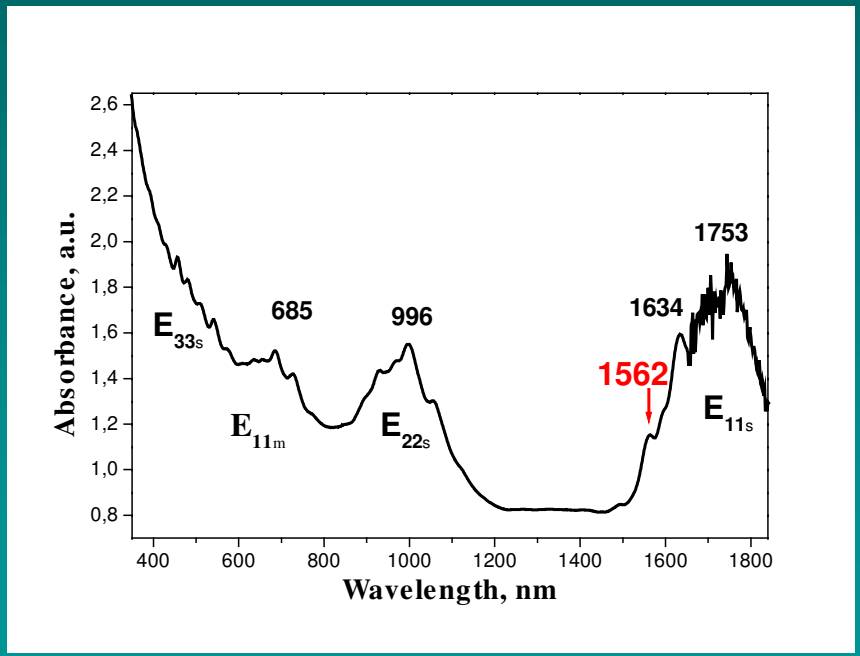
- Er^{3+} - glass λ=1.54 μm;
- YAP:Nd^{3+}- crystal λ=1.34 μm;
- Nd:$Y_{0,9}Gd_{0,1}VO_4$ - crystal λ=1.34 μm;
- Nd:$GdVO_4$ λ=1.34 μm;
- LiF - F^{2-} - crystal $\lambda\approx$1.15 μm;
- YAG:Nd^{3+} - crystal λ=1.064 μm;
- Nd^{3+} - glass λ=1.055 μm.

Er^{3+}- fiber lasers

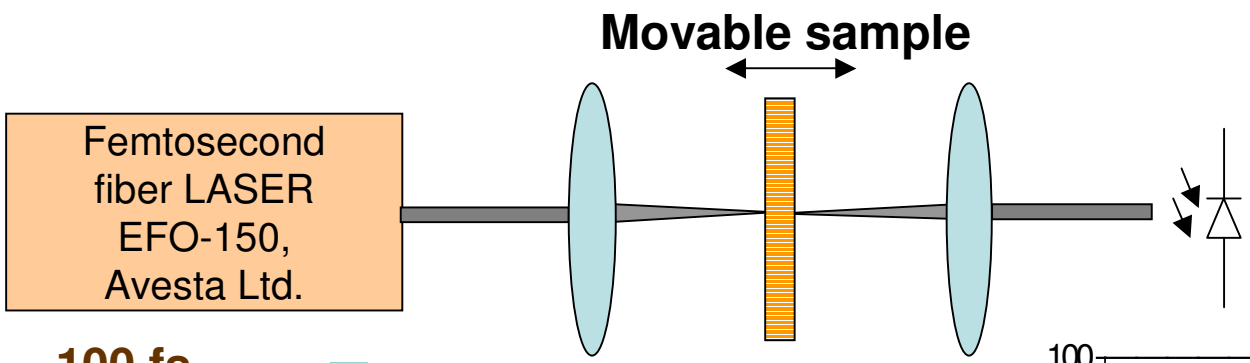
(1.54 –1.57 μm)

Saturable absorber “polymer+ arc SWNTs” for Er^{3+}- fiber laser





Z-scan measurements of saturable absorption



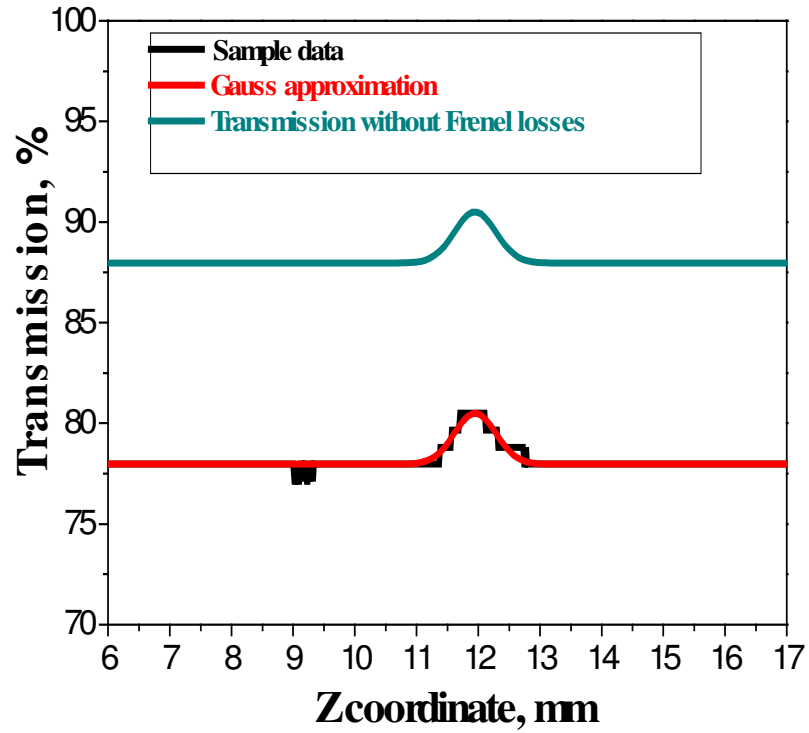
100 fs, 70MHz, 1560 nm, 10 мW

Z coordinate

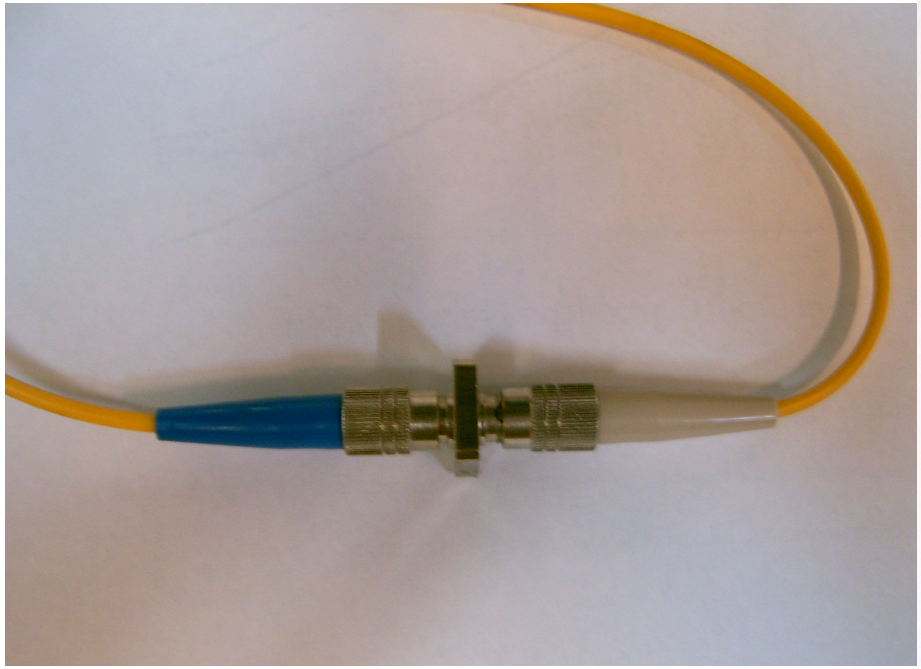
Saturable losses

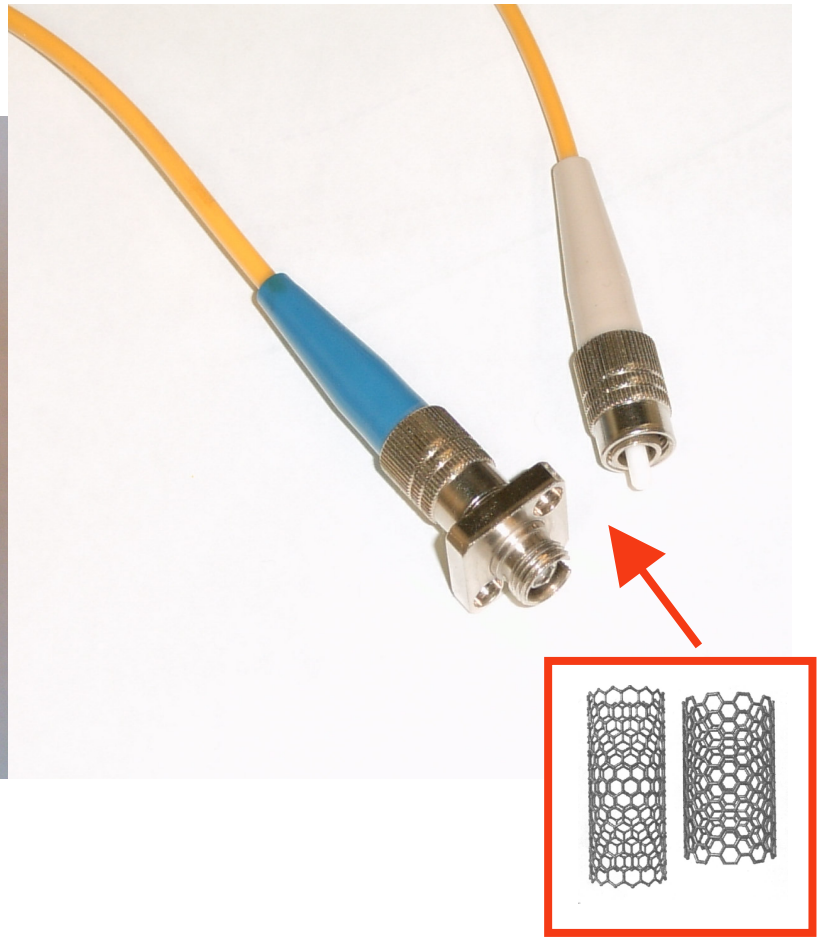
7-15%

A.V. Tausenev, E.D. Obraztsova A.S. Lobach et al., Quantum Electronics 37 (2007) N9.

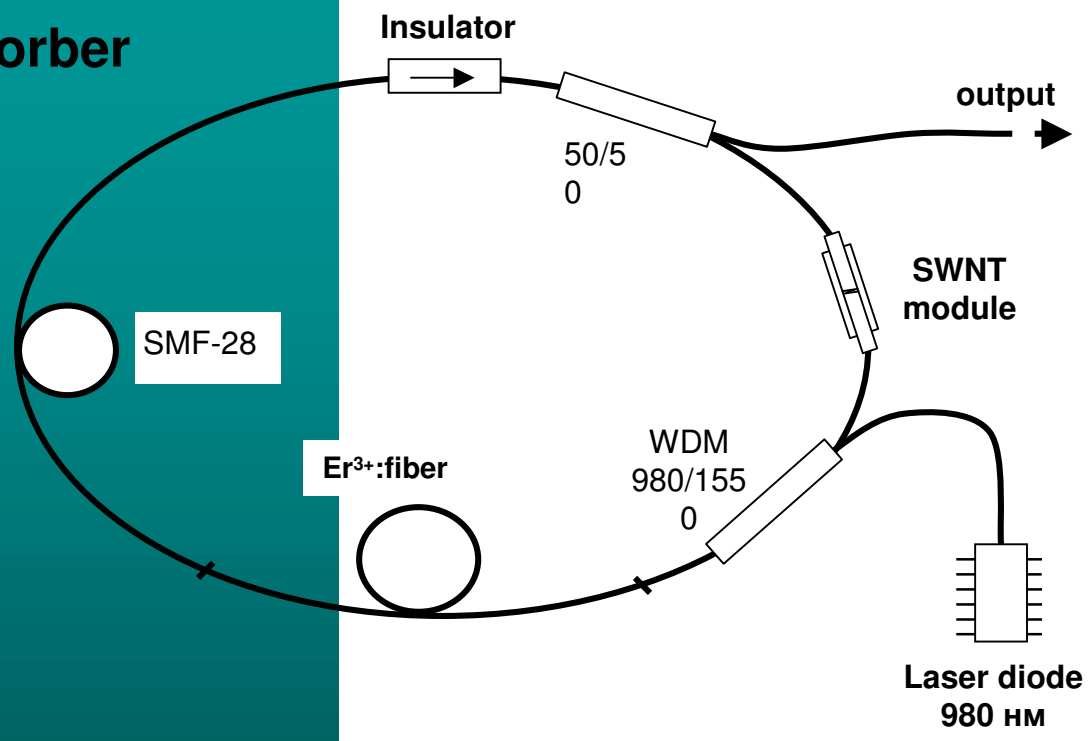


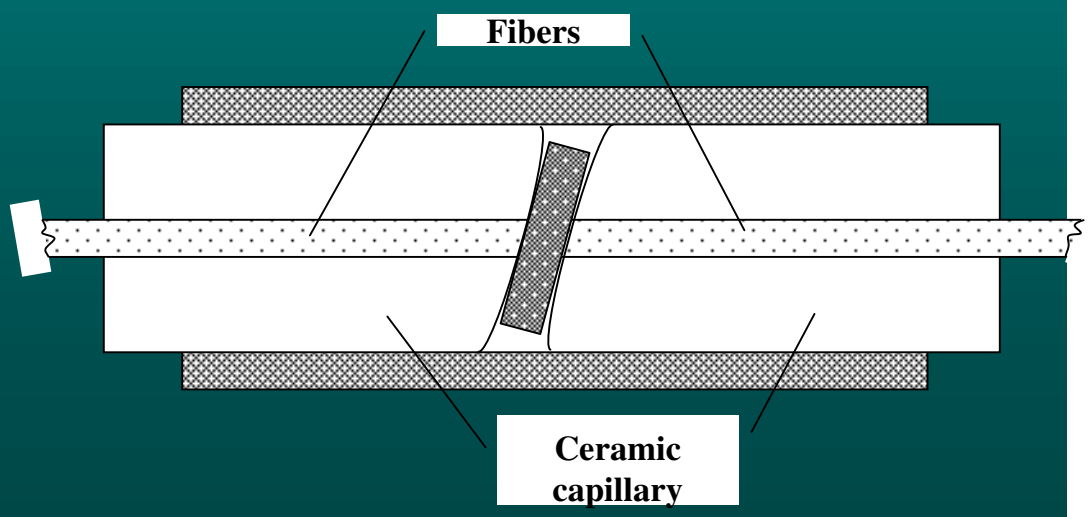
Insertion of a film-like SWNT-based absorber in the fiber





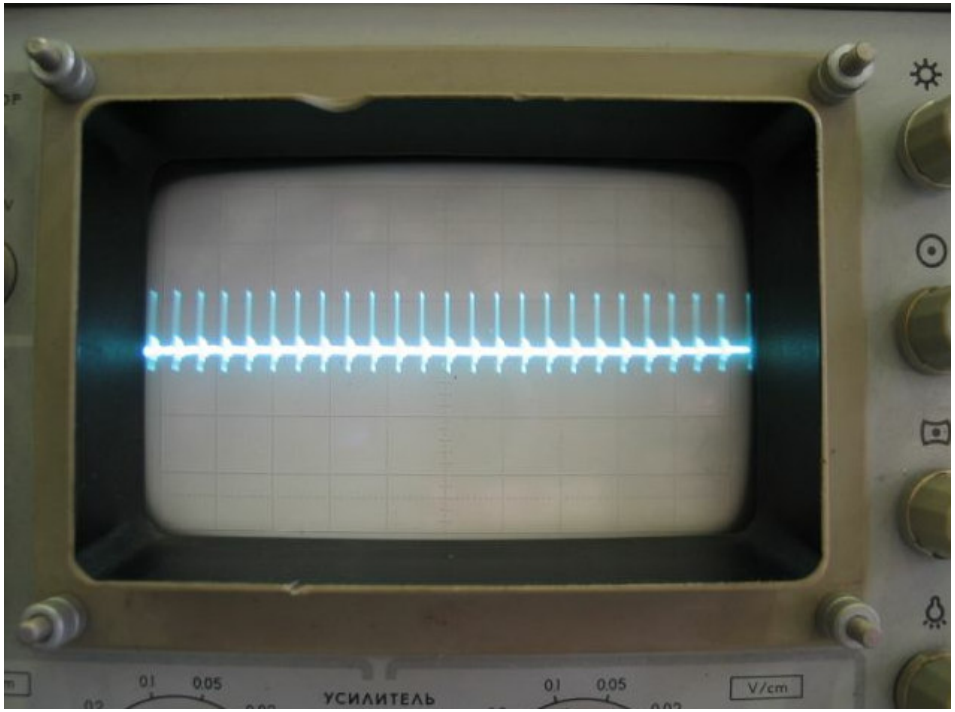
Scheme of Er^{3+}- fiber laser with a ring resonator containing a saturable absorber "arc SWNTs +PvA"

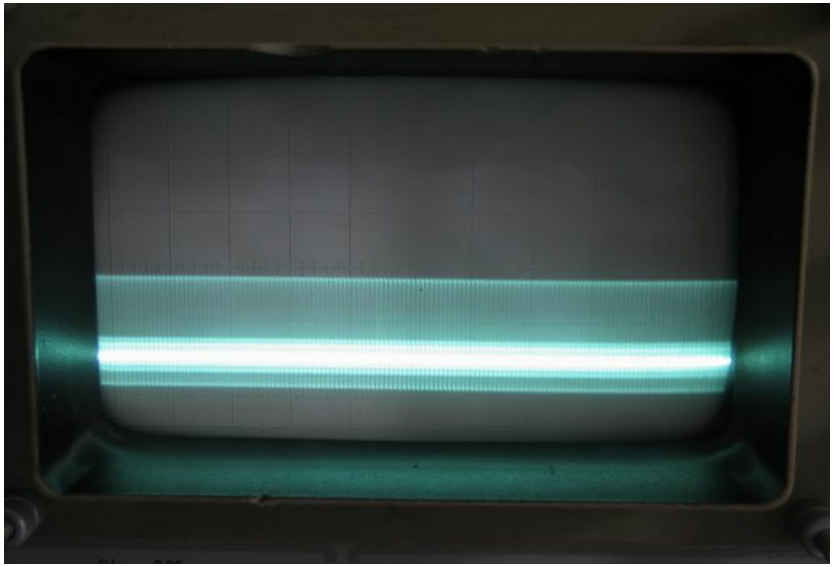




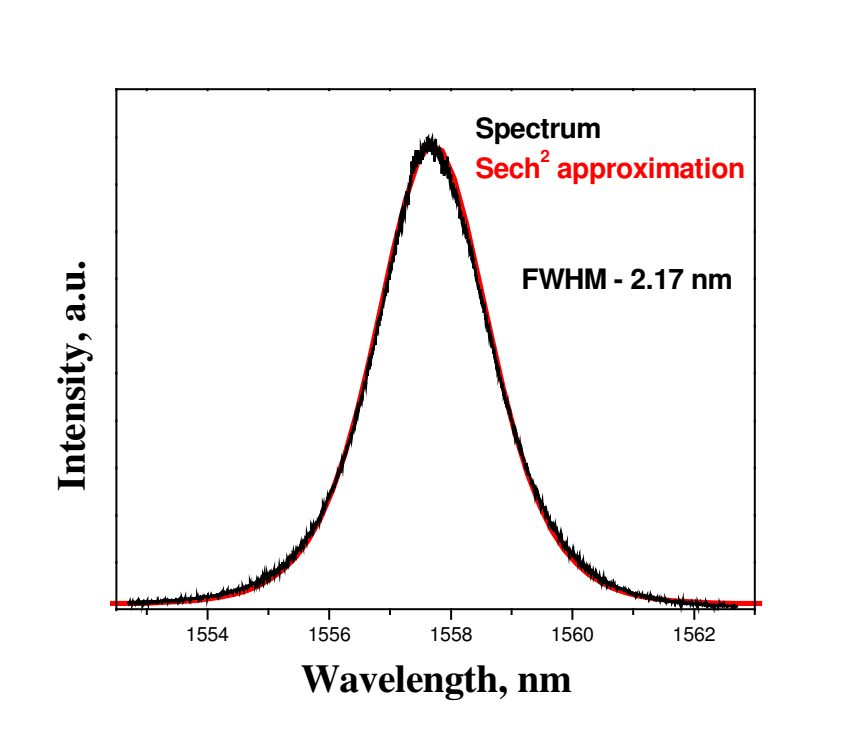
A.V. Tausenev, E.D. Obraztsova, A.S. Lobach et al., *Quantum Electronics 37 (2007) 205-208.*

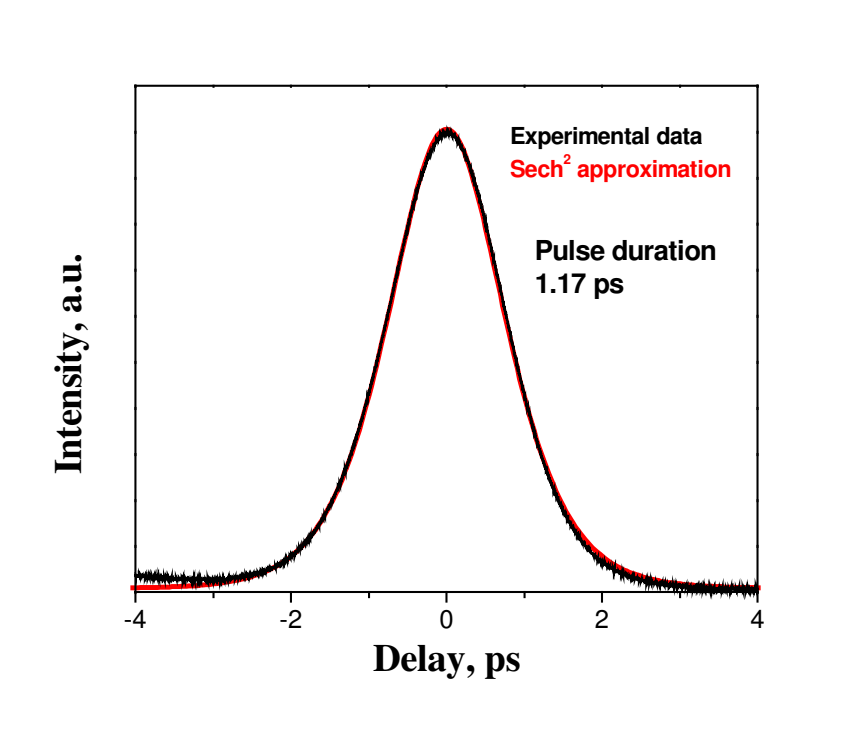
A train of sub-picosecond output laser pulses registered with PIN photodetector



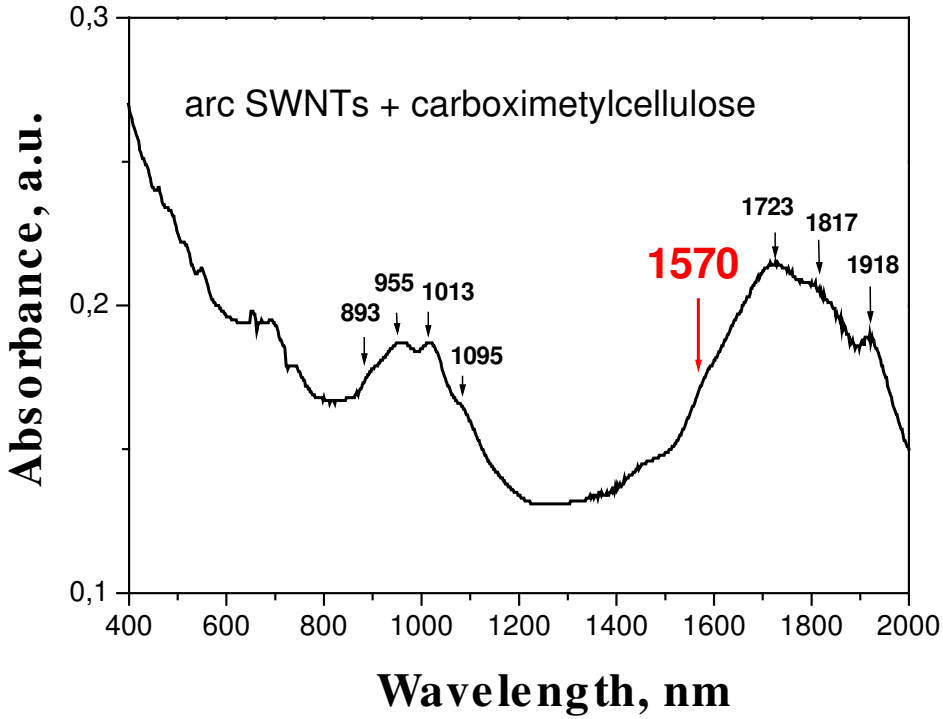


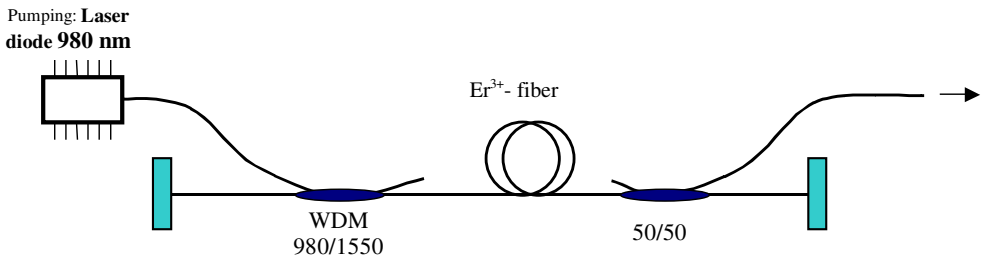
Spectrum and autocorrelation function for a single output pulse (1.17 ps) of Er^{3+}-fiber laser with a ring resonator working in the mode locking regime with the *"cellulose+arc SWNTs"* saturable absorber

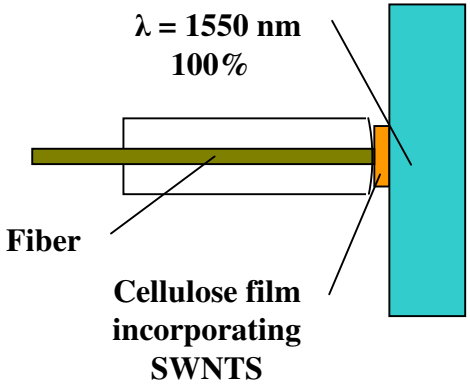




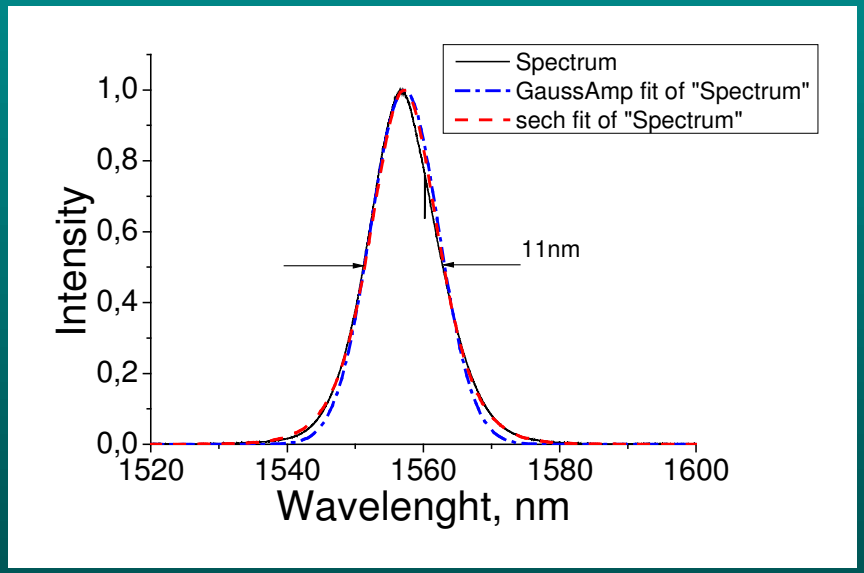
Cellulose-based saturable absorbers in the linear resonator of Er^{3+}- fiber laser

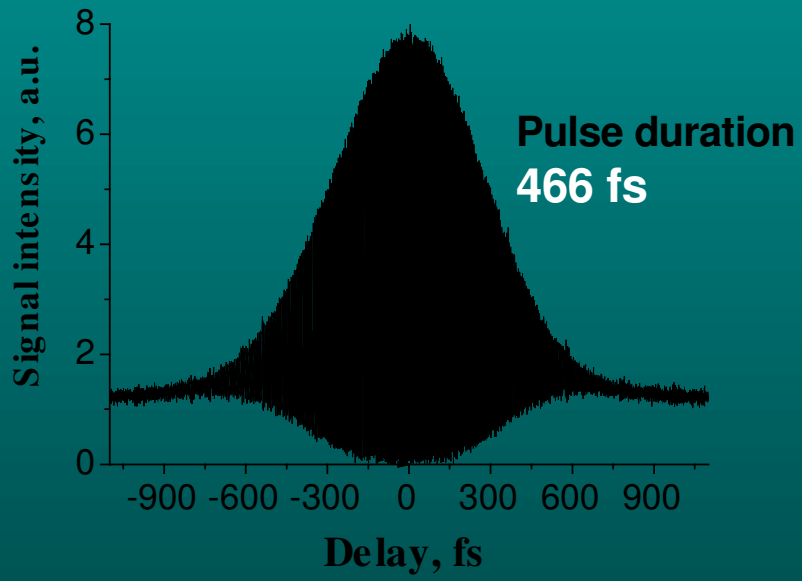






Spectrum and autocorrelation function
for a single output pulse (466 fs) of Er^{3+}-fiber laser
with a linear resonator
working in the mode locking regime
with the *"cellulose+arc SWNTs" saturable absorber*



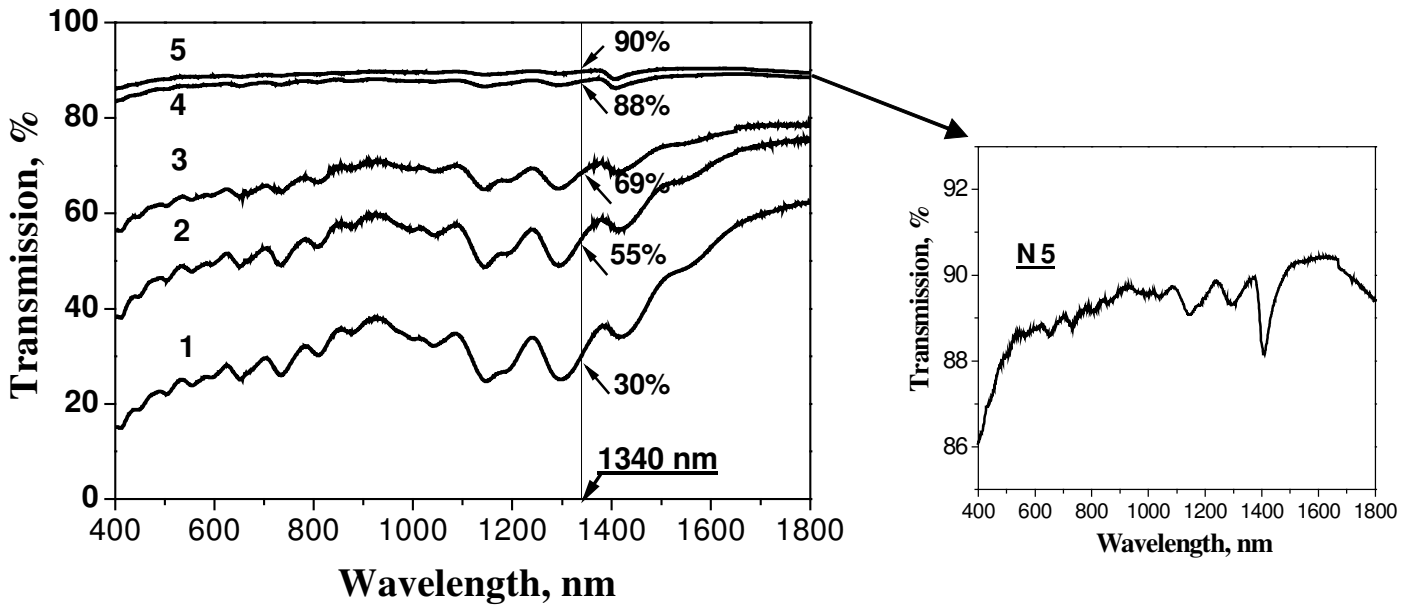


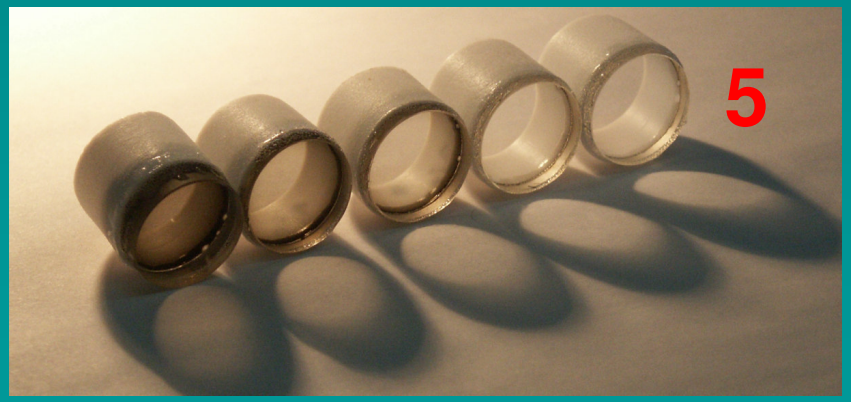
A.V. Tausenev, E.D. Obraztsova, A.S. Lobach et al., *Quantum Electronics 37 (2007) 847*

.

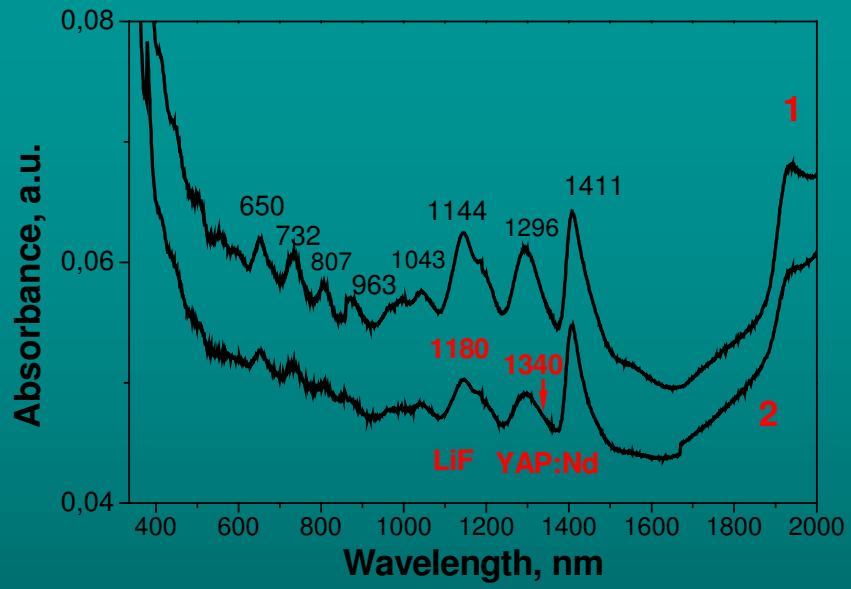
Optimization of the film and the resonator parameters

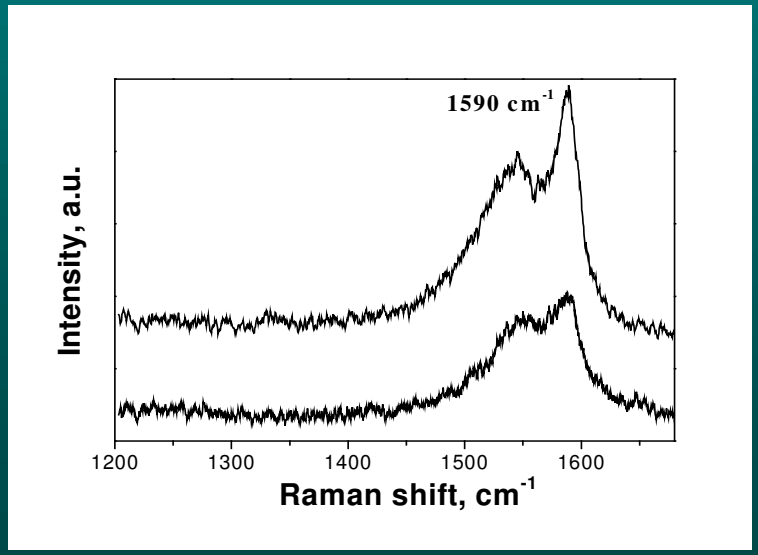
Thin films of a high optical quality with optical losses less than 5%.



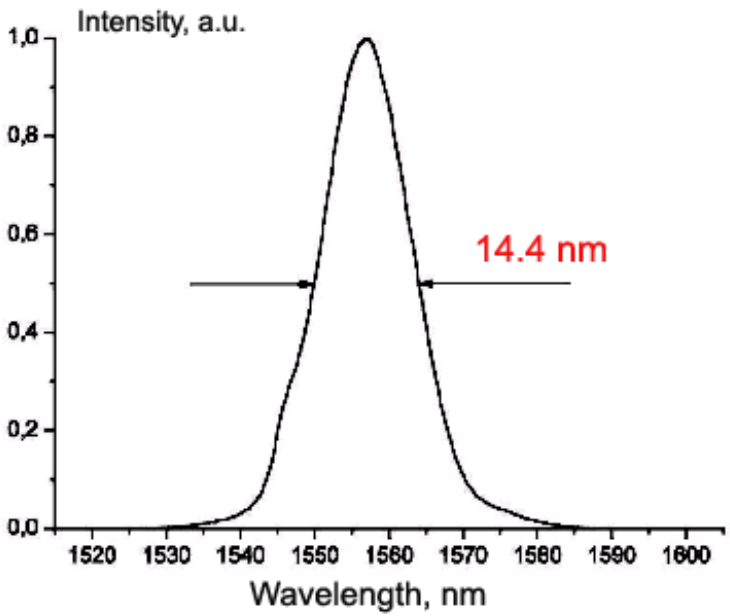


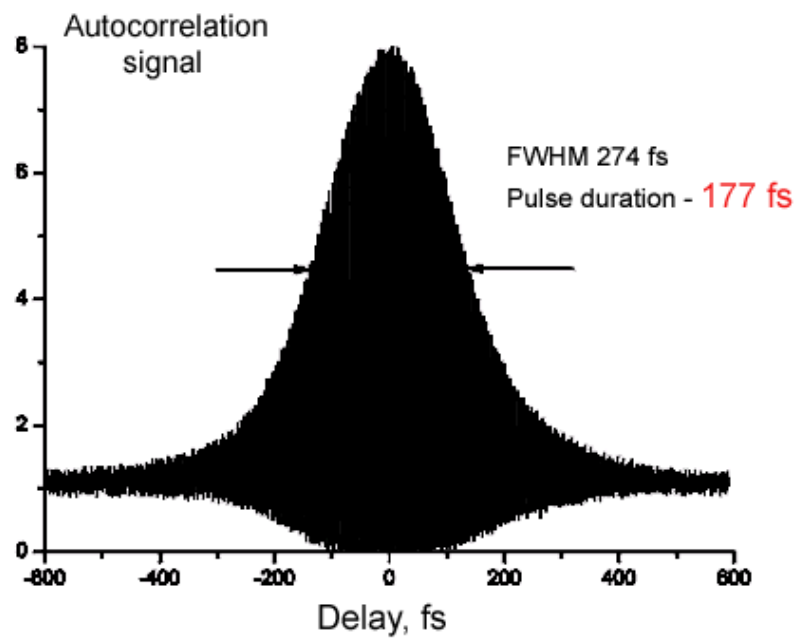
Thin films with a low optical density for formation of optical elements (mirrors, filters) in solid state lasers with bulk elements





The SWNT-based media is not a limiting factor for the pulse duration



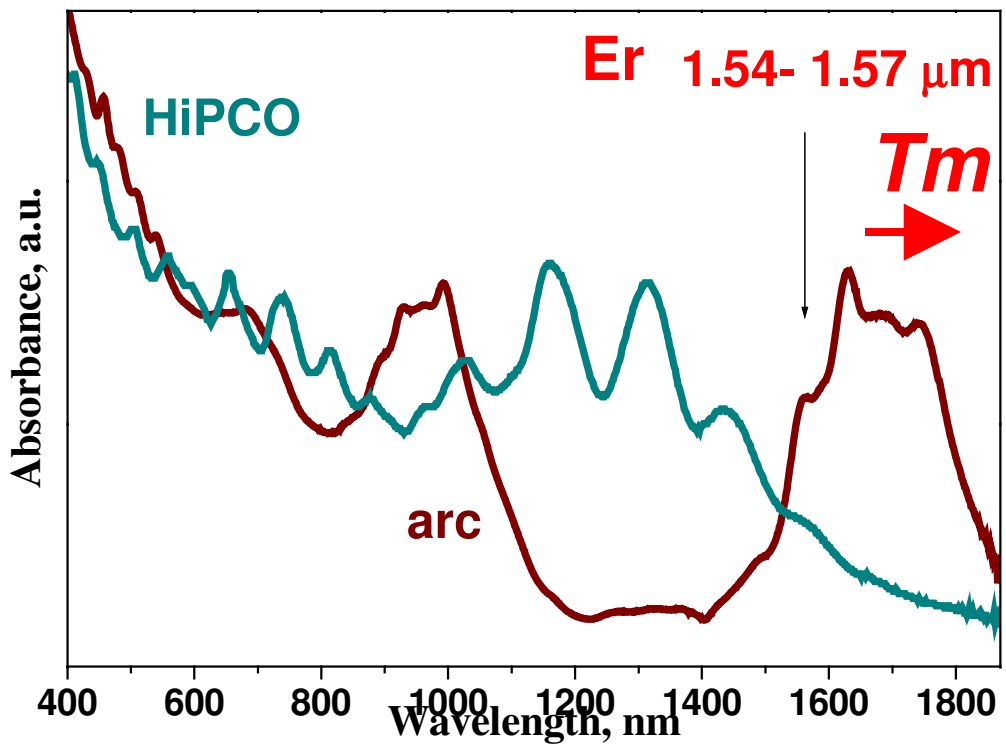


The pulse may be shortened via the resonator optimisation

A.V. Tausenev et al., *APL 92 (N18) (2008)*

Extending of the operational spectral range of fiber lasers

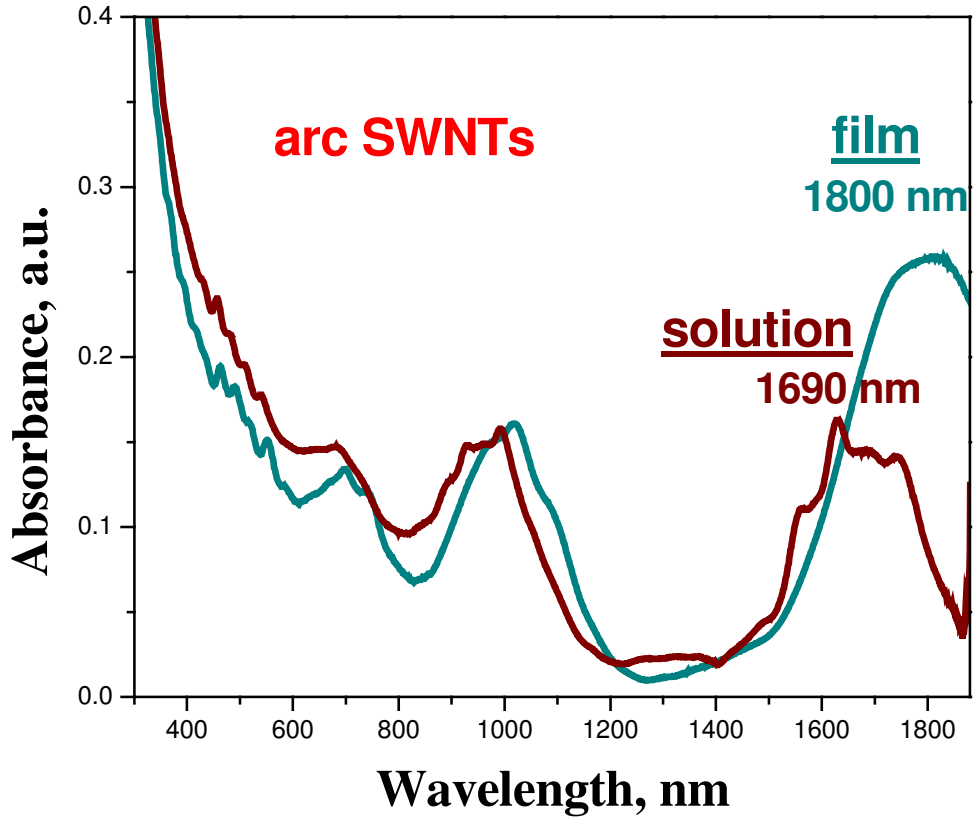
with SWNT saturable absorbers



177 fs • Er^{3+} -fiber λ=1.55-1.57 μm;

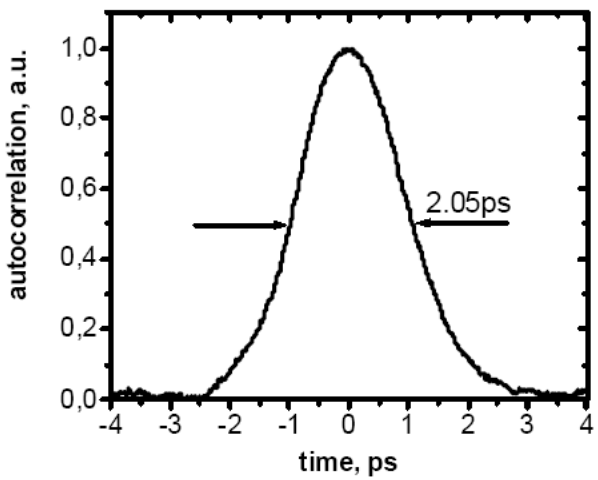
? Tm-doped fiber λ=1.7-2.1 μm

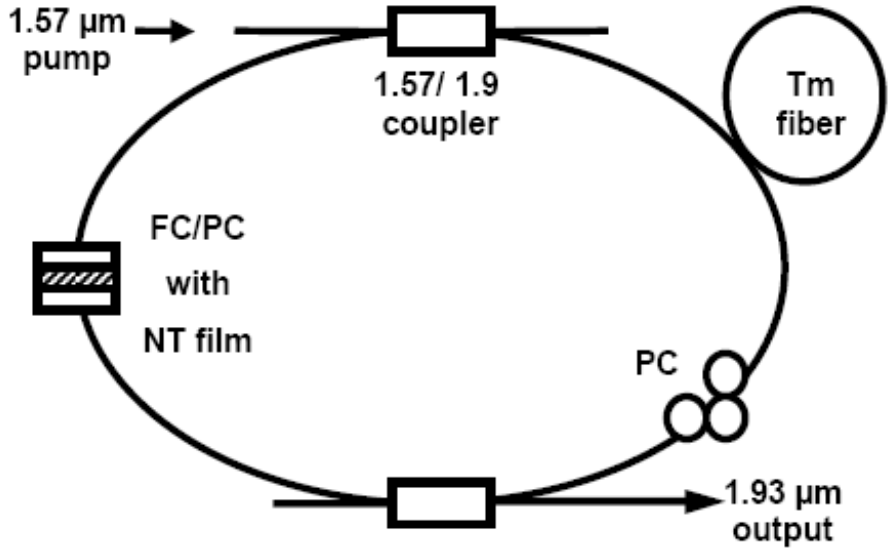
Adjustment of E_{11} absorption band parameters to the working wavelength of Tm-doped fiber laser



Realization of self-mode locking regime in thulium fiber laser with the carbon nanotube saturable absorber

1.93 μm

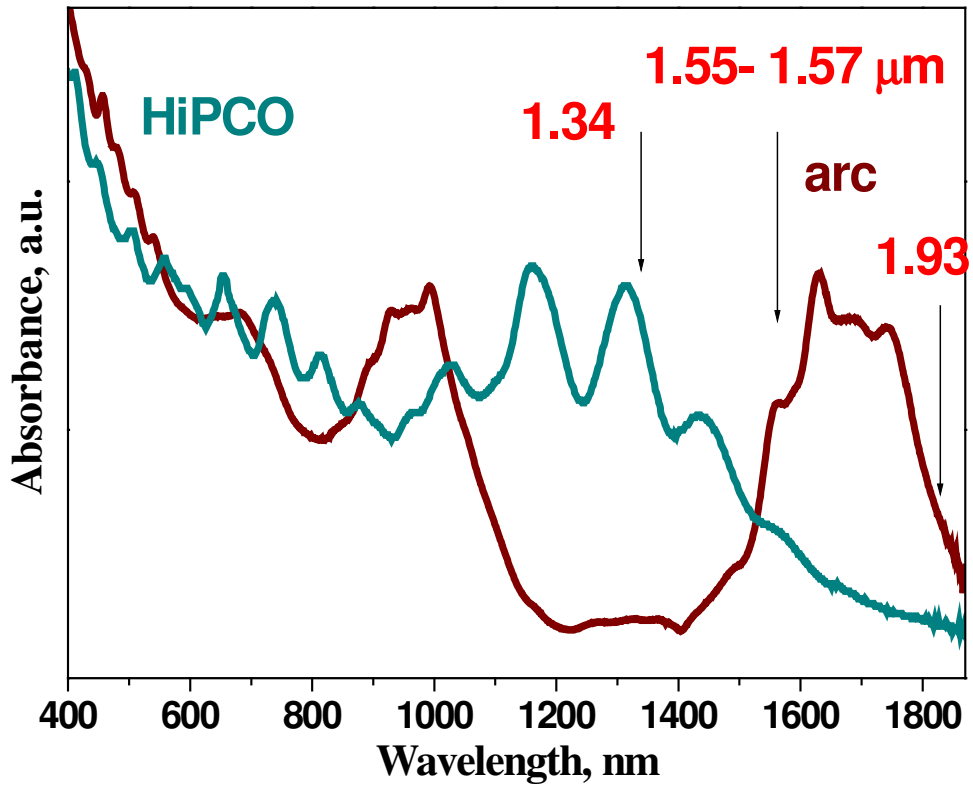




M.A.Solodyankin, E.D. Obraztsova, A.S. Lobach et al., (submitted to Optics Letters)

Need of new saturable absorbers for the spectral range 2-3 μm

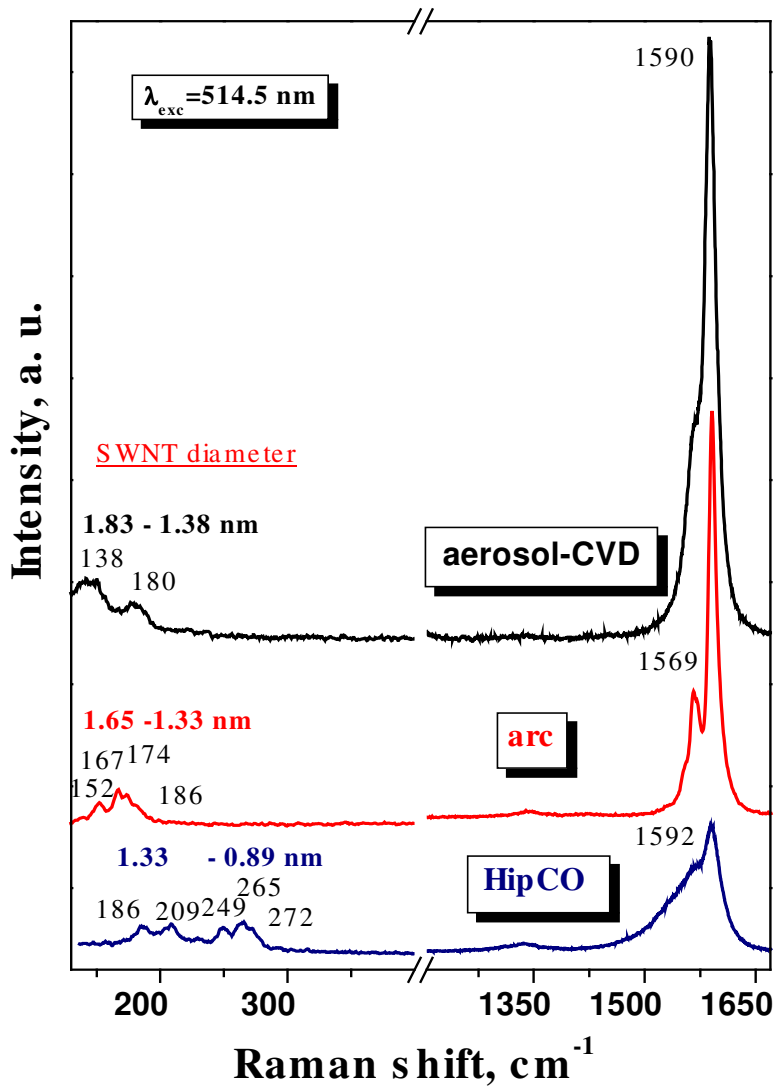
Ho, Cr, ZnSe….



2-3 μm

The bigger tubes are needed!

Raman spectra of SWNTs grown with different methods



Aerosol- CVD- ferrocene

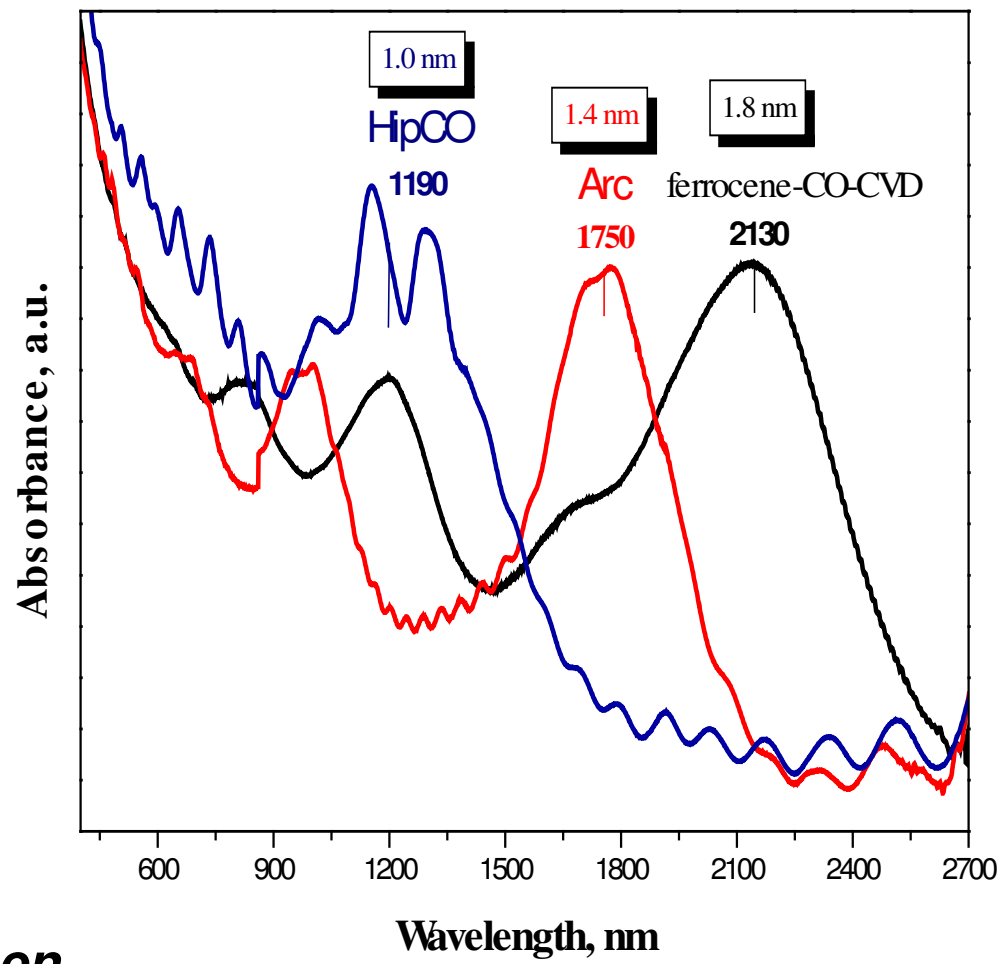
A.Moisala, A.G. Nasibulin et al. , Chemical Engineering Science 61 (2006) 4393.

UV-VIS-NIR optical absorption spectra of SWNTs grown with different methods

E.D. Obraztsova, A. I. Chernov, A. S. Lobach, A.G. Nasibulin, M. Y. Zavodchikova, E. I. Kauppinen

"CARBON NANOTUBE-BASED OPTICAL MEDIA WORKING IN SPECTRAL RANGE 1.0 - 2.5 MICROMETERS",

Proc. IWEPNM 2008, p. 146 (submitted to Physica Status Solidi).



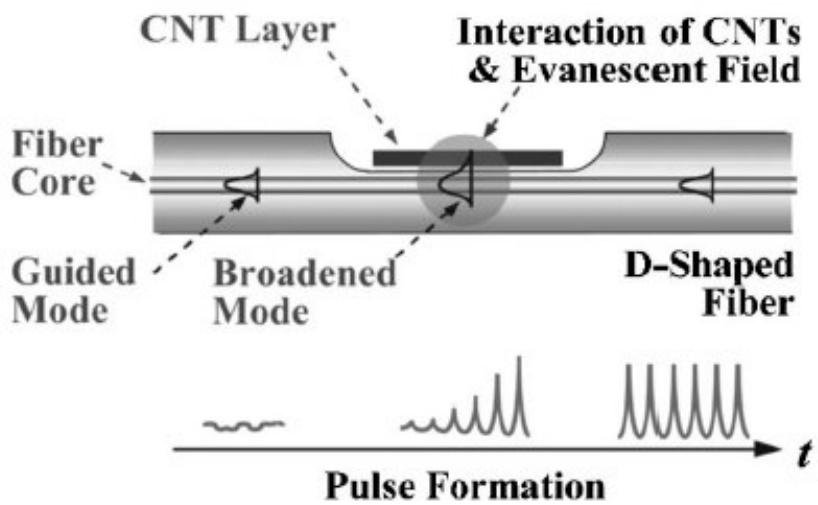
Collaboration with Group of Prof. Esko Kauppinen TKK (Helsinki)

Prospectives:

Distributed nanotube-based elements or (even) active media for lasering

1. **Development of formation technology of glasses**

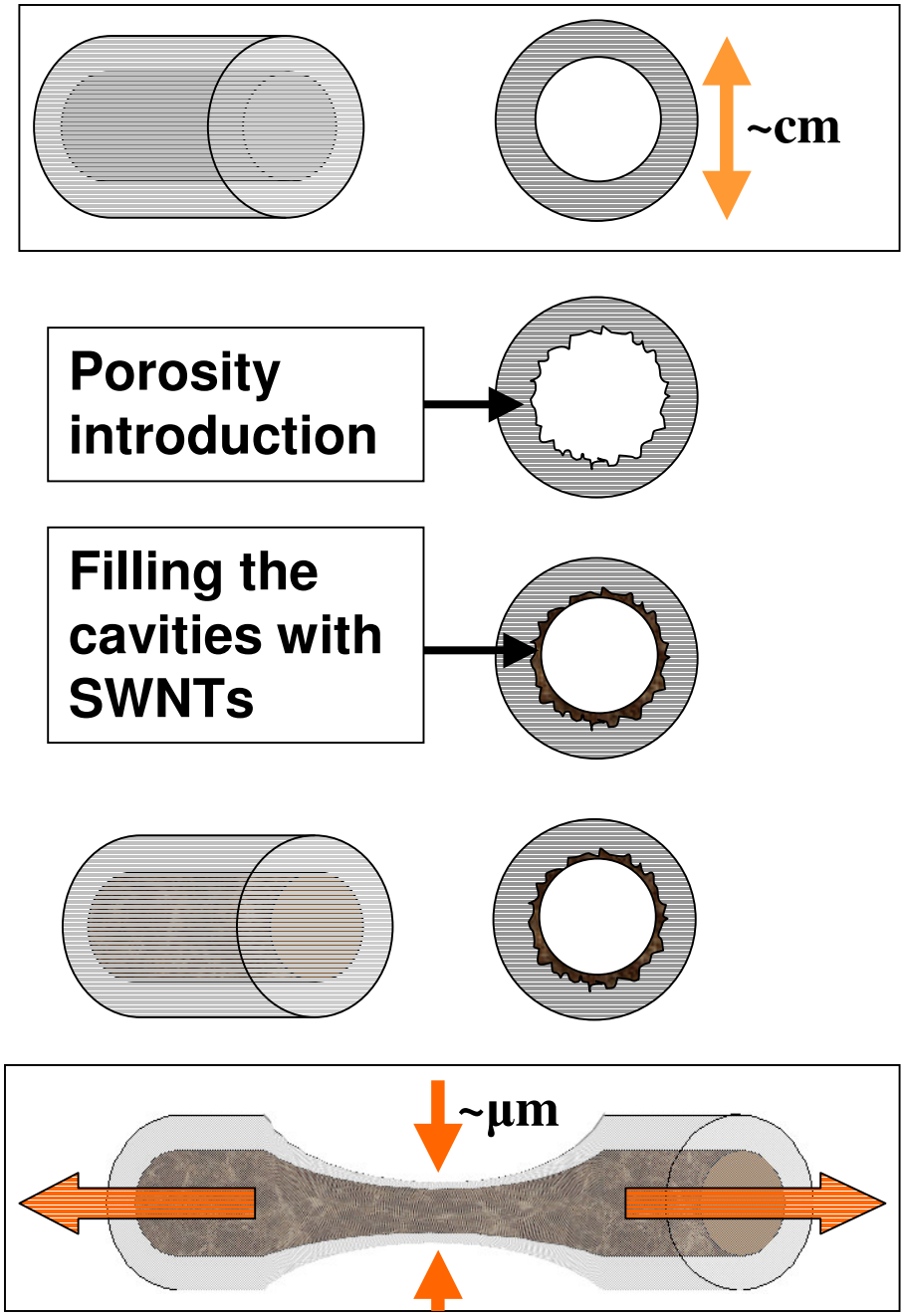
with dispersed nanotubes



2. **Introduction of SWNTs into the fiber core**

(Song et al., Optics Lett. 32 (2007)148)

D-shaped fibers



Inroduction of nanotubes into the glass fiber core during the fiber formation

CONCLUSION

Since 2003 a non-linear optics
became a field of a real technological application of
single-wall carbon nanotubes
with new remarkable results and
clear prospectives for further development.

- Optical Spectroscopy
- Electronic Properties
- Nonlinear Optics
- Electron Emission

International Workshop

"Nanocarbon Photonics and Optoelectronics"

3 - 9 August 2008

Holiday Centre «Huhmari», Polvijärvi, Finland

http://www.joensuu.fi/fysiikka/npo2008

Contacts - Prof. Yuri Svirko yuri.svirko@joensuu.fi