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Single-wall carbon nanotubes
for photonics applications

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nanotube synthesis, treatment and diagnostics

Laser experiments and discussions
Optics of nanotubes
A raw nanotube soot

Purified ropes
A pristine nanotube soot

Chemically purified nanotubes

OPTICAL MEDIA
based on single-wall carbon nanotubes

Aqueous suspensions

Polymer films

Optical elements (mirrors, filters)
A pristine nanotube soot

Optical media based on single-wall carbon nanotubes

Chemically purified nanotubes

Aqueous suspensions

Polymer films

Optical elements (mirrors, filters)
Applications

• Transparent filters
• Photoluminescent markers
• Nanotubes for lasers
Passive mode locking –
a way to produce
ultrashort laser pulses
Continuous wave laser radiation

Train of femtosecond pulses

Output radiation

Laser crystal (active medium)

Carbon nanotubes
Laser-induced transparency (saturable absorption)

Absorption

Saturation of absorption

Transparency
• 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)
Discrimination of the laser pulses of different intensity with a saturable absorber

\[ \Delta I_{\text{out}} \]

\[ \Delta I_{\text{in}} \]

SA
Self mode-locking: regularization of the laser output and generation of ultrashort pulses

**Laser output without** the saturable absorber

**with** the saturable absorber

\[ t_1 \approx 10 \times 2L/c \]

\[ t_2 \approx 100 \times 2L/c \]
Regularization of the laser output due to discrimination of laser modes with different intensity

Random phases

Mode locking

(simulation, number of modes 6)

(simulation, number of modes 6)
Since 2004, a mode-locking regime with the saturable absorbers based on CARBON NANOTUBES has been realized in a number of solid state lasers:
Wavelength “windows” for optical communications

- Nd³⁺ - glass: 1.06 μm
- YAG:Nd³⁺ - crystal: 1.06 μm
- LiF:F⁻ - crystal: 1.17 μm
- Tm-doped fiber: 1.99 μm
- Tm:YAlO₃: 1.99 μm
- Ho:YAG-crystal: 2.1 μm
Laser surgery
*(especially- ophtalmology)*
Laser diagnostics of contaminations in atmosphere
Time-resolved spectroscopy

- Nd:GdVO$_4$ - 1.34 µm
- YAP:Nd$^{3+}$ - crystal - 1.34 µm
- Er$^{3+}$-glass - 1.52-1.57 µm
- Tm-doped fiber - 1.93 µm
- Tm:YAlO$_3$ - 1.99 µm
- Ho:YAG-crystal - 2.1 µm
CARBON NANOTUBES (!!!):

- Universal (1-3 $\mu$m spectral range)
- Fast (sub-picosecond)
- Long-living (years)
- Low “switch on” threshold (25 mW)
- High damage threshold (>1x10^9 W/cm^2)

saturable absorber
The element introduced into the laser cavity should have a high optical quality – to keep the generation.

**Tasks:**

1. **To create** such materials.
2. **To perform a complex optical characterization** of such materials.

- linear optical absorption
  - photoluminescence
  - spontaneous Raman scattering
- non-linear Z-scan (non-linear absorption)
  - pump-probe
Formation of carbon nanotubes of different geometry

\[ C = n \cdot a_1 + m \cdot a_2 \]
Formation of single-wall nanotube (6,3) from the graphene sheet
UltraViolet- Visible- Near-InfraRed (UV-VIS-NIR)
Optical Absorption
Two-dimensional electron dispersion in graphene

\[
E(K) = \pm \gamma_0 \left\{ 1 + 4 \cdot \cos \left( \frac{\sqrt{3} \cdot K_x \cdot a_0}{2} \right) \cdot \cos \left( \frac{K_y \cdot a_0}{2} \right) + 4 \cdot \cos^2 \left( \frac{K_y \cdot a_0}{2} \right) \right\}^{1/2}
\]
Kataura-plot:
dependence of the electron transition energy on nanotube diameter

H. Kataura et al.,
Synth. Metals 103 (1999) 2555
Hexagonal Boron Nitride

- B
- N
Density of one-electron states in graphene and in single-wall carbon nanotube
A.V. Osadchy, E.D. Obraztsova et al.,
JETP Letters 77 (2003) 405-410
A typical UV-VIS-NIR optical absorption spectrum of an ensemble of Individual single-wall carbon nanotubes

An average diameter and a diameter distribution
A “fingerprint” Raman spectrum of single-wall carbon nanotubes

Measurement of non-linear absorption
Saturable absorption
(Z-scan measurements)

Transmission, %

Z coordinate, mm

Sample data
Gauss approximation
Transmission without Frenel losses
Time-resolved measurements – pump-probe method
Absorbance change in a SWNT film as a function of delay between pump and probe pulses.

Collaboration with Prof. Yury Svirko (Joensuu University, Finland)
From a real nanotube material to optical media
Synthesis of single-wall carbon nanotubes by the **electric arc technique**

To isolate the semiconducting nanotubes, the ropes should be disintegrated!
Aqueous suspensions of single-wall carbon nanotubes of optical quality

Method *(SDBS, DOC)*


Ultracentrifuging

(acceleration > 100 000 g)

Powerful ultrasonication
A typical UV-VIS-NIR optical absorption spectrum of an ensemble of individual single-wall carbon nanotubes.
UV-VIS-NIR optical absorption of aqueous suspensions of single-wall carbon nanotubes, synthesized by different methods.
Photoluminescence of aqueous suspensions of single-wall carbon nanotubes

$\lambda_{\text{exc}} = 532 \text{ nm}$

- HipCO SWNTs
- arc SWNTs

PL Intensity, a.u.

Wavelength, nm

800 1000 1200 1400 1600

976 1026 1119 1176 1258 1382 1492 1589 1.38 nm
Formation of ultrashort laser pulses with carbon nanotubes
A first mention about using *the SWNTs as a saturable absorber*


**SAINT- Saturable Absorber Incorporating NanoTubes**
Non-linear optical properties of carbon nanotube suspensions
Non-linear transmission ($\lambda=1.54 \mu m$) of HipCO single-wall carbon nanotubes in aqueous suspension of SDBS/D$_2$O

N.N. Il’ichev, E.D. Obraztsova, S.V. Garnov, S.E. Mosaleva,

*Quantum electronics 34 (2004) 572*
Mode locking in Er\textsuperscript{3+}-glass laser ($\lambda=1.54 \text{\mu m}$)

N.N. Il’ichev, E.D. Obraztsova, S.V. Garnov, S.E. Mosaleva,

Operational spectral range of solid state lasers, working in mode-lock regime with Liquid nanotube-based saturable absorbers

- Er\(^{3+}\) - glass, \(\lambda=1.54 \ \mu\text{m}\);
- YAP:Nd\(^{3+}\) - crystal, \(\lambda=1.34 \ \mu\text{m}\);
- LiF - F\(^2\) - crystal, \(\lambda\approx1.15 \ \mu\text{m}\);
- YAG:Nd\(^{3+}\) - crystal, \(\lambda=1.064 \ \mu\text{m}\);
- Nd\(^{3+}\) - glass, \(\lambda=1.055 \ \mu\text{m}\).
Polymer films incorporating single-wall carbon nanotubes
Formation of SWNT-containing polymer films

PvA or + SWNTs = cellulose

Liquid cast on a smooth substrate followed by a slow drying
Mode-locking in YAP:Nd\(^{3+}\) laser with a film-like polymer saturable absorber containing SWNTs

Solid elements are preferable for bulk solid state lasers!!!

The fiber lasers are **compact and easy integrated.**

*The new elements should have these properties.*
Carbon Nanotube-containing polymer films for FIBER LASERS
Saturable absorber “polymer+ arc SWNTs” for Er$^{3+}$- fiber laser

PvA and carboximethylcellulose
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 train of sub-picosecond output laser pulses registered with PIN photodetector
The SWNT-based media is **not** a limiting factor for the pulse duration.

The pulse may be shorten via the resonator optimisation.

A.V. Tausenev, E.D. Obraztsova et al., *APL 92 (N18) (2008)171113*
Optimization of the optical media parameters
Optical losses
Thin films of a high optical quality with optical losses 5-80%.

![Graph showing transmission vs. wavelength with various curves and transmission percentages at specific wavelengths like 1340 nm.](image-url)
Optical elements based on single-wall carbon nanotubes
Efficiency = coincidence of the medium absorption maximum with the laser working wavelength
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

Separation of single-wall carbon nanotubes over diameter.

Narrow fractions → a high efficiency.

Quantum efficiency of photoluminescence in narrow fractions is about 15%
(instead of 0.1% in ensembles)
Density gradient centrifugation – a way to get nanotube fractions with a narrow diameter distribution

M. S. Arnold, A. A. Green, M. C. Hersam et al., Nature Nanotechnology 1, 60-65 (2006).
Nanotubes with narrow diameter distributions
A.I. Chernov, E.D. Obraztsova,

K.Yanagi, Y. Miyata, and H. Kataura,
A. Green, M. Hersam, NanoLetters 8 (2008) 1417
Metallic SWNTs in suspension after density gradient centrifugation

Metallic SWNTs in thin films

Absorbance, a.u. vs. Wavelength, nm

- E_{11metal}
- E_{22sem}
- Absorbance peaks at 698, 664, 697, 960, 1018, 1.37 nm, 1.47 nm, 1.51 nm
Extension of the *working spectral range*
Demand of new saturable absorbers for the spectral range 2-3 $\mu$m

Ho, ZnSe....

The bigger tubes?
Ferrocene-aerosol-CVD technique

Collaboration with Prof. Esko Kauppinen (TKK, Helsinki)

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

E.D. Obraztsova, A.I. Chernov et al., NDNC conf., Taiwan May 2008
Demand of new saturable absorbers at wavelengths **less than 1 \( \mu \text{m} \)**

The smallest tubes – diameter 0.3-0.4 nm – \( E_{11} \) absorption at 850 nm

\( E_{22} \) instead of \( E_{11} \)
Carboxymethylcellulose + arc SWNTs

1.06 \mu m
Yb-based fiber laser operating at 1.06 µm


PROSPECTIVES
Nanotube-based active media?
Introduction of nanotubes into the fiber core during the Fiber formation
Conclusion

Single-wall carbon nanotubes and media based on them can be efficiently used as universal saturable absorbers providing the sub-picosecond pulses formation in a wide class of bulk and fiber solid state lasers working in the spectral range 1-3 µm.
We are not alone…..

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


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

2007 – introduction SWNTs into the fiber core (Song et al., Optics Lett. 32 (2007)148)

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

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