Comparison of Optoelectronic Properties of Doped and Pristine Nanotubes Based on Carbon and Tungsten Disulfide

Maksim Paukov, Anastasia Goldt, Gennadiy Komandin, Alexander Syuy, Dmitriy Yakubovskiy, Sergei Novikov, Alexander Polyakov, Reshef Tenne, Alla Zak, Albert Nasibulin, Aleksei Arsenin, Valentyn Volkov, Maria Burdanova
e-mail: paukov.mi@phystech.edu

Introduction

Aim: investigation of the optical and terahertz features of carbon (C) and tungsten disulfide (WS_2) nanotubes (NT) and tuning of these properties by p-type doping with $HAuCl_4$ (gold nanoparticles)
Approach: geometry of given samples was studied by transmission and scanning electron microscopy (TEM and SEM respectively), their optoelectronic features were examined via Raman spectroscopy, absorption spectroscopy in ultra-violet and visible range, and terahertz spectroscopy in time domain (TDS).

Organic and inorganic Nanotubes

- Both CNTs and WS_2NTs are theoretically constructed by rolling up a 2D sheet of the corresponding material to form a single-walled or multi-walled cylinder (Fig. 1).

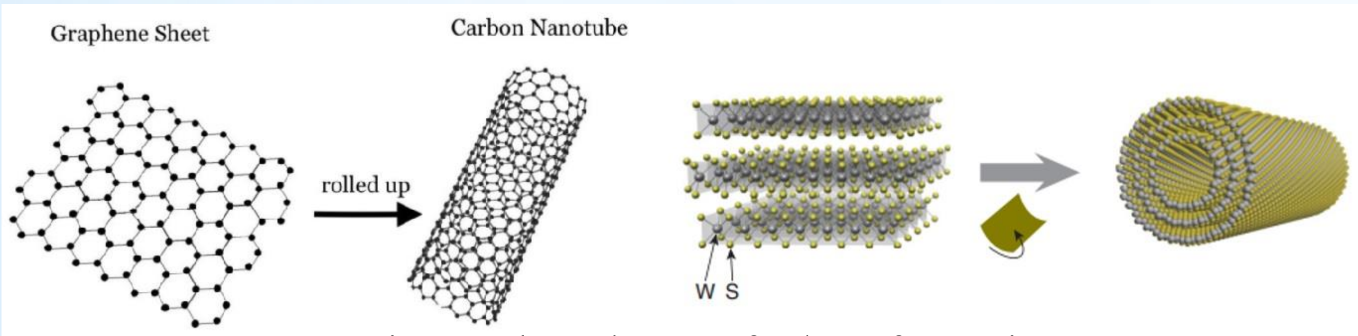

Fig. 1. The scheme of tubes' formation.

- Regardless of the production method, 2/3 of obtained CNTs demonstrate metallic behavior and 1/3 - semiconducting, whereas WS_2NTs are semiconducting ones.
- P-doping shifts the Fermi level of the materials, allowing to control their optoelectronic properties.

Sample preparation

- CNTs films were synthesized using the aerosol method
- WS_2NTs films were produced from commercially-available powder (NanoMaterials Ltd) using vacuum filtration method

Microscopy characterization

The morphology of studied samples was investigated using TEM and SEM.

- The TEM images showed that CNTs tend to form **bundles** due to the interactions via Van der Waals forces. The averaged diameter of the bundle was 8.9 nm while the mean diameter of individual NT - 1.8 nm. The averaged length is >10 μm.
- WS_2NTs appear to be **multi-walled** and have a wider diameter distribution of 79.6 nm. The SEM images allowed to determine the mean length of WS_2NTs, which is 1.3 μm.

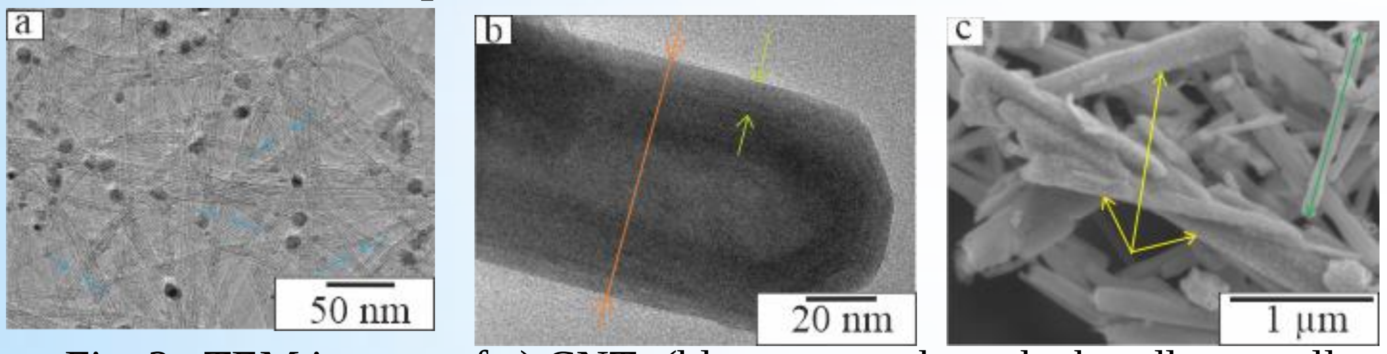

Fig. 2. TEM images of a) CNTs (blue arrows show the bundles, small particles are catalysts) and b) typical individual WS_2NT (the orange line shows the diameter, light green arrows - the thickness of NT's walls); c) SEM image of doped WS_2NT (yellow arrows indicated NT dotted with gold nanoparticles, green arrow shows the typical length).

Optical properties

When the energy of incident photons matches these transitions the resonant enhancement of photophysical processes such Raman scattering, Absorption, and others are expected to be seen.

- As it can be seen, the p-doping influences the position and lessens the intensity of **Raman active modes**. Compared to their 2D-counterparts, the NT show a difference of the resonant frequencies, which can be explained by the **strain and curvature** of the tube's structure. Doping with $HAuCl_4$ results in the shift towards higher frequency in both CNT and WS_2 NT which indicates p-doping.

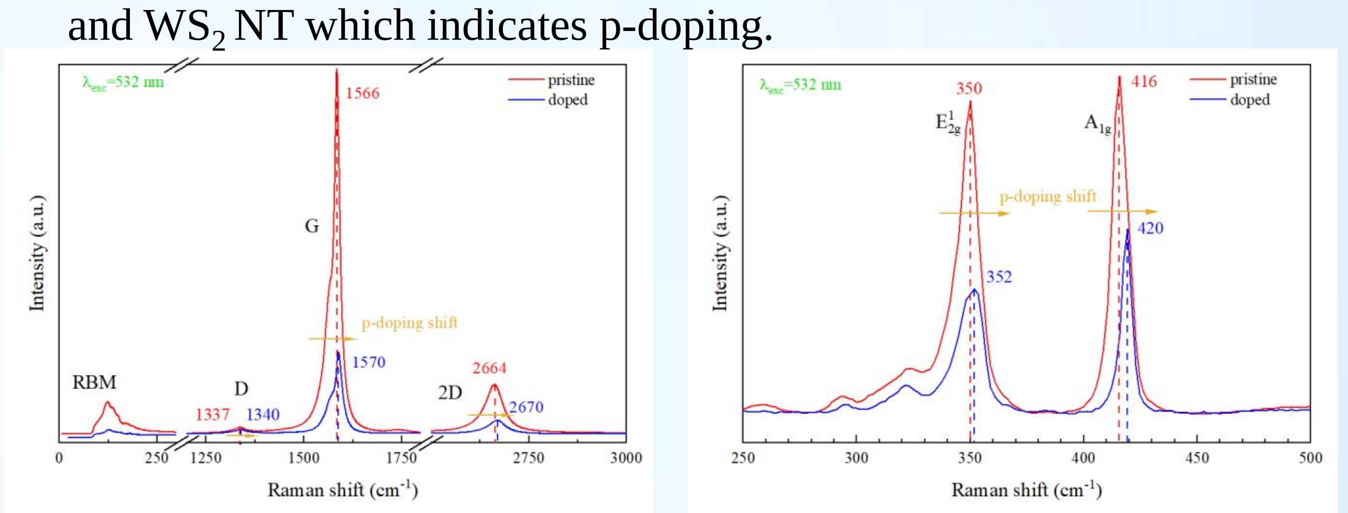

Fig. 3. Raman spectra of CNT (right) and WS_2NT (left).

- The absorption spectroscopy allowed us to detect the **excitonic transitions** in the NT as well as the impact of p-doping on shifting the Fermi level. Compare to their 2D analogues, NTs demonstrate a shift in the position of these transitions.

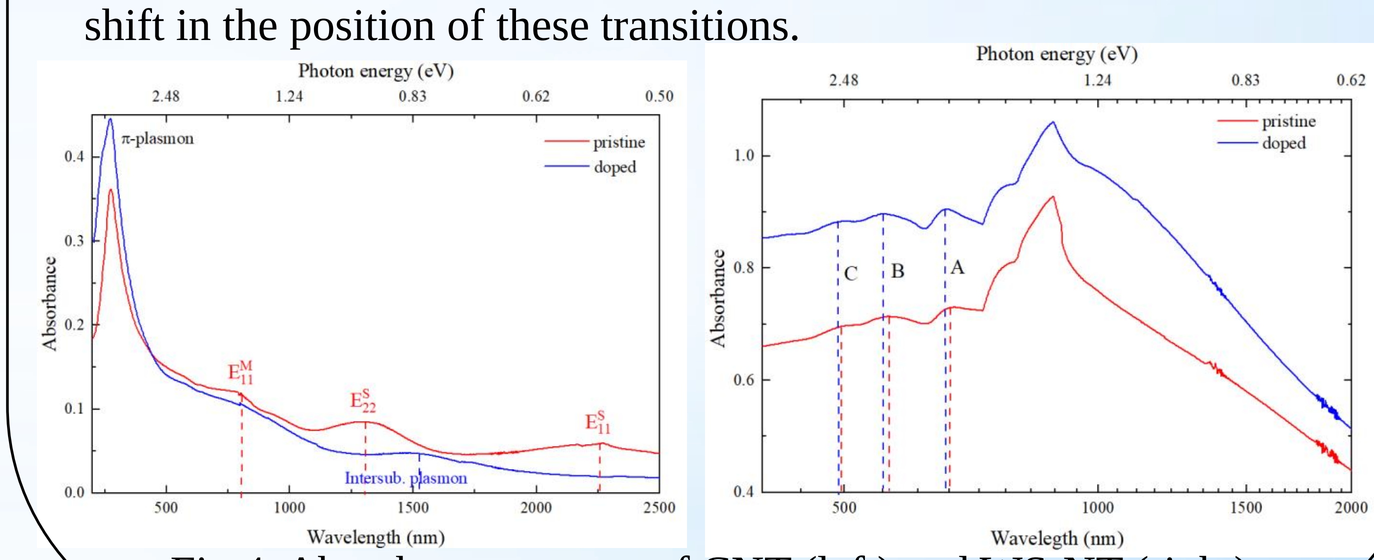

Fig.4. Absorbance spectra of CNT (left) and WS_2NT (right).

Terahertz spectroscopy

Both types of NTs appear to have two contributions in their conductivity:
1) a **Drude** component, responsible for the motion of **free charges** in the presence of the electric field;
2) a **Lorentz** component, which describes the localized state of **axial plasmons**.

The peak, corresponding to axial plasmon, is red-shifted for WS_2NTs compared with CNTs due to the difference in the length. Doping leads to the broadening of the conductivity due to the additional free charges.

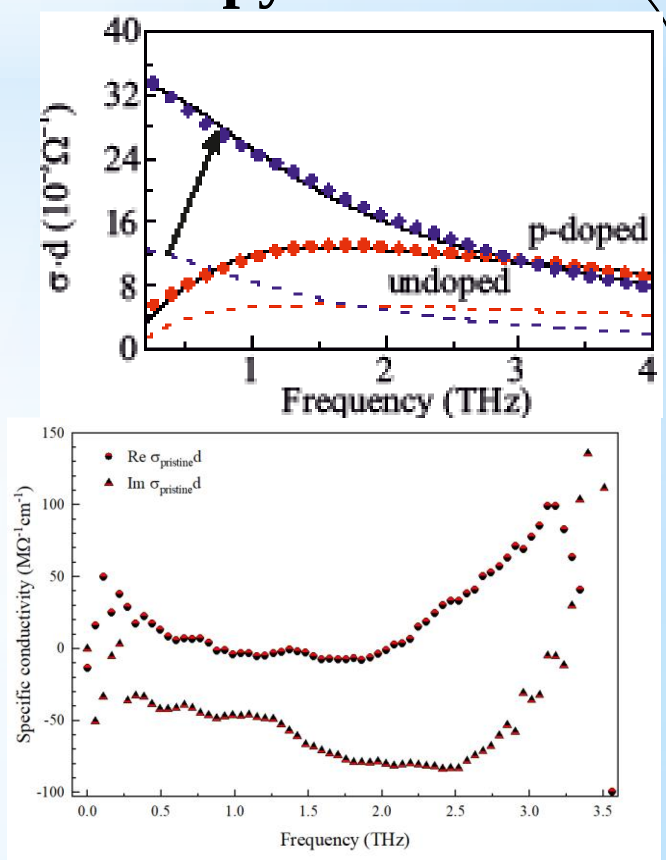

Fig.5. Terahertz conductivity of CNT(top) and WS_2NT(bottom).

Conclusions

Overall, NT possesses the optoelectronic properties that are changed because of the curvature, quantum confinement, and localization. Doping with $HAuCl_4$ results in tunability of all optoelectronic properties.

Future plans

Different length and diameter WS_2NT with different morphology are to be investigated to understand the origin of the conductivity peak in THz region.

Acknowledgements

This project is supported by Russian Science Foundation (No. 21-79-10097), Ministry of Science and Higher Education of the Russian Federation (No. 075-15-2021-606), and Russian Foundation for Basic Research (No.18-29-27010 MK).

MIPT Skoltech GPI RAS

References

1. Burdanova M. G., et.al., A Review of the Terahertz Conductivity and Photoconductivity of Carbon Nanotubes and Heteronanotubes. Adv. Optical Mater., 2021, 210104.
2. Sinha S.S., et. al., MoS2 and WS2 Nanotubes: Synthesis, Structural Elucidation, and Optical Characterization. J. Phys. Chem. C, 2021, 125 (11), 6324-6340.