

Proceeding Paper

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

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Abstract: The optoelectronic properties of one-dimensional nanomaterials play an important role in electronic devices. In the present work, pristine and doped Carbon Nanotubes (CNTs) and WS₂ Nanotubes (WS₂NT) are investigated by using absorption, Raman, and THz time-domain spectroscopy (THz-TDS). We demonstrate that the one-dimensional materials share similar properties associated with curvature and location in comparison with two-dimensional materials. In addition, we show how doping influence to these properties. Our results pave the way toward the application of such materials as a prospective material for optoelectronic devices including future wireless communication devices.

Keywords: inorganic nanotubes; tungsten disulfate nanotubes; absorption; Raman spectroscopy; terahertz time-domain spectroscopy

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1. Introduction

The family of two-dimensional (2D) semiconducting transition metal dichalcogenides (TMDs) such as MoS₂, WS₂, MoSe₂ and others has grown significantly [1]. TMDs exhibit strong absorption in the visible range and show promise for next-generation optoelectronic devices. It comes from tightly bound excitons with binding energies on the order of several hundred millielectronvolts [2,3]. These excitons appear as a consequence of quantum confinement and reduced dielectric screening that enhances the Coulomb interactions between electrons and holes. The further enhancement of these properties can be achieved by reduction of the dimensionality by the formation of nanotubes from similar materials. Following the discovery of carbon nanotubes (CNTs), inorganic nanotubes (NT) from the TMDCs were reported. These materials might be used in a number of real applications in the field of tribology, machining, nanophotonics, and nanooptics [4,5].

Noble metal-TMDs NT has unique properties due to the size-dependent properties of both NT and metal nanoparticles [6]. Being semiconducting, TMDs NT decorated with

gold and silver nanoparticles are of particular importance because of the tunability of optoelectronic properties. Previously, optical properties of WS₂NT were partially studied [5].

In this article, we the deposition of thin WS₂NT by vacuum filtration and CNT by dry-transfer technique is implemented. Except for the standard characterization methods (TEM, SEM, UV-Vis-IR spectroscopy, Raman), we also present transmission measurements in the THz range (0.2 THz to 3 THz). The experimentally observed dependencies are described by establishing the relation between the size of both types of NT and electromagnetic response. The comparison between different material NTs is given.

2. Methods

The samples were prepared from commercial WS₂NT, produced by NanoMaterials Ltd. in ethanol suspension. After sonication, the thin films were obtained by the vacuum filtration method using a nitrocellulose membrane. The obtained films were transferred to the z-cut quartz substrates and dissolved with acetone. The thin CNT films were obtained by the aerosol synthesis method and transferred to the same z-cut quartz substrates by using the dry transfer technique [7].

Scanning Electron Microscope (SEM) imaging was performed with a high-resolution SEM Zeiss Ultra with a secondary electron detector, an acceleration voltage of 5.0 kV, and a working distance of 6.0 mm. Transmission Electron Microscopy (TEM) imaging was performed using JEOL JEM-2100. Figure 1 shows representative TEM and SEM images of the WS₂NT and CNT films. The NT dimensions are detailed in Table 1. TEM and SEM images allow us to estimate the averaged diameters and length of NT are detailed in Table 1.

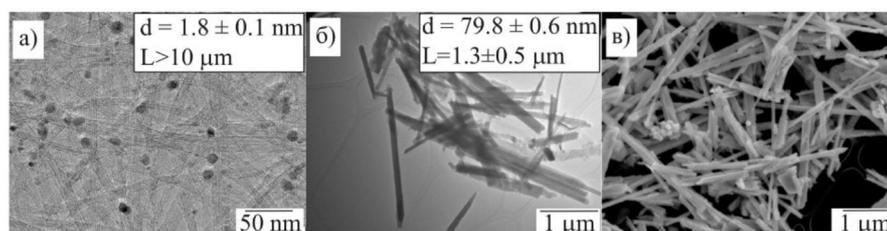


Figure 1. TEM images of (a) CNT and (b) WS₂NT samples. SEM image of WS₂NT.

Table 1. NT dimensions.

Sample	Diameter (nm)	Length (μm)
CNT	1.8	>10
WS ₂ NT	79.8	1.3

The choice of 1 mm-thick quartz substrate meant that the THz spectral resolution was not reduced substantially in comparison to the THz spectral resolution for the spectrometer in addition to its transparency in this frequency range. Equilibrium absorbance spectra were determined via homemade THz time-domain spectroscopy (0.2–3 THz range), and a Cary 5000 UV/VIS/NIR spectrophotometer (250–2500 nm). For Raman spectra a confocal micro-spectrometer (Labram, Jobin-Yvon Horiba) with a 520 nm laser at 0.58 mW (with spectral resolution 1 cm⁻¹ and spatial resolution 1.5 μm) was used. For the chemical doping, pristine WS₂NT and CNT films were drop-coated with HAuCl₄ ethanol solution. After 20 s the solvent had completely evaporated. Samples were stored in air and measured over a period of weeks.

3. Results

It is known, that the optical properties of CNT and WS₂NT samples depend on the diameter. The optical absorbance of the CNT showed characteristic strong peaks of excitonic transitions in semiconducting (E^S₁₁, E^S₂₂) and metallic (E^M₁₁) NT in the absorption

spectra on the wavelengths of 2300, 1240 and 870 nm respectively. These excitonic transitions corresponds to the CNTs with the diameter of 1.8 nm. For WS₂NT the peaks on 670, 560 and 500 nm correspond to the direct A, B and indirect C excitonic transitions. The intensive peak at about 730 nm corresponds to a Mie scattering originating from surface plasmon resonance. The comparison with the results in paper [5] allows to conclude that all absorption peaks are red-shifted by 47 nm with respect to WS₂NT of diameter 36 nm. This observation comes in agreement with the larger diameter in the investigated sample proved by TEM.

A large change in absorbance occurs upon adsorption doping with HAuCl₄. Because of this CNT chemical potential has lowered, depleting the valence bands of electrons, suppressing the excitonic optical absorption transitions. An additional absorption peak arose between 1000 and 2000 nm which can be attributed to intersubband transitions. The shift of the excitonic peaks for doped WS₂NT after doping was also observed. The driving force for the mentioned electron transfer occurs from the difference between the Fermi level of WS₂NT and CNT and a rather high reduction potential of HAuCl₄.

Raman spectra showed typical Radial breathing modes (RBM) of CNT with the diameter of 1.8 nm, what is also in agreement with the TEM data. WS₂NT are characterized with two peaks, corresponding to longitudinal (E_{2g}) and transversal (A_{1g}) phonon modes with the wavelengths of 417 and 351 cm⁻¹ respectively. These modes are shifted by 1 and 5 cm⁻¹ with comparison to the one layer 2D WS₂, and 2 and 4 cm⁻¹ with comparison to the multilayer 2D WS₂ [7], which is explained by the NT curvature influence on oscillating lattice modes. Doping with HAuCl₄ results in the shift towards higher frequency in both CNT and WS₂ which indicates p-doping.

Finally, the real and imaginary parts of the equilibrium sheet terahertz conductivity of CNT and WS₂NT films were obtained. The increase of the real part of the CNT conductivity towards lower frequencies is caused by the contributions of the free charges absorption, described by the Drude-model, and axial plasmons, described by the Lorentz model [8]. The conductivity of WS₂NT, on contrary, increases towards higher frequencies, which evidences the presence of axial plasmons with the resonant frequency in far or middle infrared region. Doping leads to the broadening of the real part of the conductivity of the CNT with the simultaneous increase of the amplitude. Meanwhile, in WS₂NT the shift of the conductivity towards higher frequency was observed due to the same reason.

4. Conclusions

The structure and optoelectronic properties of doped and pristine CNT and WS₂NT were examined by numerous techniques such as absorption, Raman, and THz time-domain spectroscopy. Overall, WS₂NT possesses the optoelectronic properties that are changed because of the curvature, quantum confinement, and localization in comparison to their 2D counterparts. Doping with HAuCl₄ results in tunability of all optoelectronic properties.

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