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Broadband Optical and Terahertz Properties of Atomically Thin 1D van der Waals Heterostructures †

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Abstract: Van der Waals (VdW) heterostructures built of atomically thin 2D material crystals exhibit unique optical and electronic properties. Here, we present a complete study of optical properties of novel 1D van der Waals heterostructures comprising carbon nanotubes (CNT) wrapped by atomically thin nanotubes of boron nitride (BN) and molybdenum disulfide (MoS_2NT). The ellipsometry measurements allowed us to retrieve of dielectric functions and the excitonic properties of such a material. The extinction peaks appear at a slightly lower wavelength compared with the excitons in the absorption curve. This could provide the evidence of the coupling effect in hollow nanotubes. In addition, the charge carrier effect which is evident from XPS measurement results in the change of the THz conductivity spectra. The study of this work provides guidance for the design of 1D van der Waals heterostructures for use in nanoscale optoelectronic devices

Keywords: nanotubes; van der Waals heterostructures; ellipsometry; terahertz

1. Introduction

Two-dimensional (2D) materials, as emerging ultrathin material families, exhibit diverse optical, electronic, such as flexible energy band design, strong Coulomb interactions, efficient luminescence and spin-valley physics, that make them ideal candidates for optoelectronic device applications. Heterostructures build of atomically-thin 2D materials show unique properties associated with their interlayer coupling and charge transfer, opening up new possibilities for the development of nano optoelectronic devices [1].

While the study of 2D heterostructures has already undergone rapid progress, the novel 1D heterostructures has been started to attract the attention. In particular, 1D van der Waals heterostructures has already showed unique properties associated with intertube coupling effect, flexoelectricity in addition to unique optoelectronic properties. Here, we report, the optoelectronic properties of novel 1D van der Waals heterostructures.

2. Sample preparation

Single-walled CNTs were synthesized via the floating-catalyst aerosol CVD method, creating 20 nm-thick films. A mean diameter of 2.1 nm was determined from transmission electron microscopy (TEM) of a number of individual tubes, while tube lengths were above 10 µm. As-deposited films were used in order to avoid additional processing steps (such as sonication and surfactant wrapping) which can introduce additional defects, change the chemical and dielectric environment, and reduce the length of the as-grown CNTs. Hence, the films contained a mix of one-third of metallic and two-thirds of semiconducting SWCNTs with a mix of chiralities. Free-standing films were obtained by a dry-transfer technique, and were used as a matrix for BN and MoS_2 NT growth by CVD. The pristine CNT film was preheated at 1050 ℃ in Ar/H_2 for 1 hour at low pressure and coated by BNNTs at 1050 ℃ (1-3 hr) at low pressure, and subsequently cooled slowly to room temperature. The MoS_2 growth was performed at 550 ℃ at low pressure, and also cooled slowly to room temperature. As-grown the outer BNNT and MoS_2 were evenly distributed in chirality.

3. Results

We obtained optical constants of C@BNNT and C@BN@MoS_2NT films using spectroscopic ellipsometry (Figure 1 a and b). In addition, the transmittance, reflectance, and absorbance of our samples were also measured. In absorption experiments appeared excitonic transitions are red-shifted with respect to the monolayer and bulk MoS_2. The extinction peaks measured by ellipsometry appear at a slightly lower wavelength compared with the excitons in the absorption curve indicating a coupling effect in hollow nanotubes.

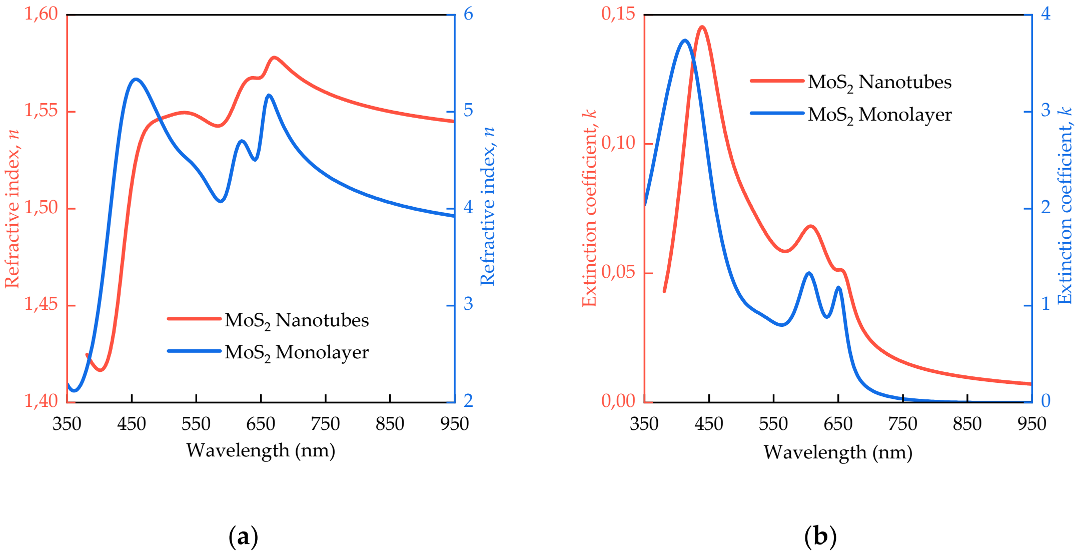
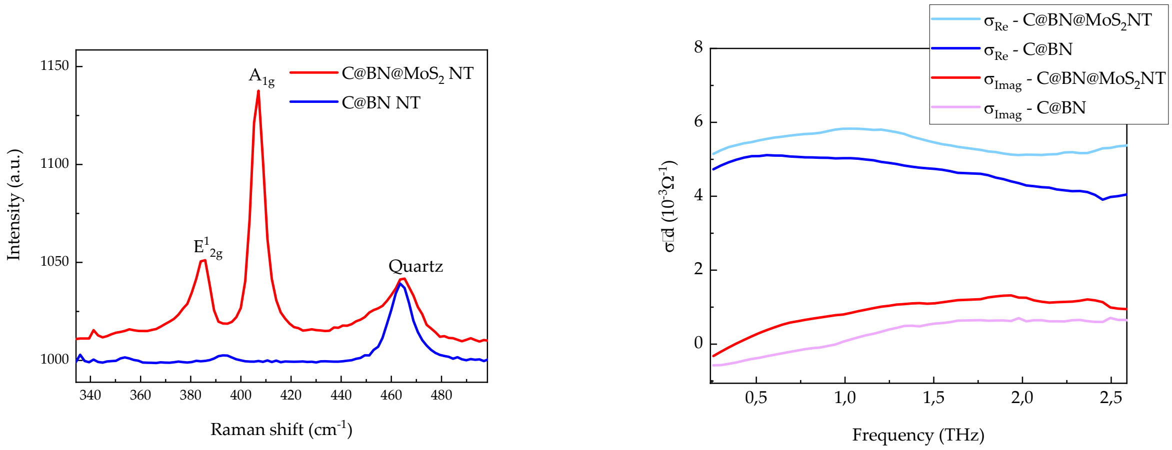


Figure 1. The refractive index (**a**) and extinction coefficient (**b**) of MoS_2 Nanotubes and Monolayer.

For the C@BN@MoS_2 NT film the in-plane and out-of-plane modes revealed by Raman spectroscopy, are in agreement with theoretical predictions for MoS_2 NTs and different to monolayer and bulk flakes (Figure 2 a). The observed rise in a real part of the THz conductivity towards lower frequency for the C@BN NT film is consistent with previous studies of CNT films with a similar morphology, where the THz conductivity contains a contribution from Drude-like free-carrier absorption and from axial plasmons.



(**a**) (**b**)

Figure 2. Raman (**a**) and THz (**b**) spectrum of 1D van der Waals heterostructures.

MoS_2 NT creates a small increase in conductivity of C@BN@MoS_2 NT across the THz range in comparison to the C@BN NTs (Figure 2 b). This extra conductivity may be originated by free charges in the outer MoS_2 NT if the as-grown material is doped. Alternatively, the MoS_2 NTs may have altered the conductivity of the encapsulated CNTs, either as a result of a strain-induced change in their band structure or by a small but finite charge transfer from the outer MoS_2 NTs to the inner CNTs. In addition, the shift of plasmonic peak may be originated by shortening of the conductivity pathways of CNTs.

The observed change in the THz conductivity has a correlation with XPS measurements [2]. The binding energy shifts in XPS spectra for core level electrons have been used previously to identify the charge transfer processes between different nanotubes in a heterostructure. The binding energy shifts can be associated with Fermi level shifts and indicates the doping as the result of charge transfer.

Finally, we used an infrared pump, visible probe spectroscopy to selectively create excitons in the carbon nanotubes, while probing the response of the A and B excitons in the MoS_2 nanotubes [2,3]. As a result, we observe a rapid and strong excitonic response of the MoS_2 NT under this below gap experiment. Optical pump-THz probe spectroscopy allows the presence of free, unbound charges in a heterostructure to be uniquely established.

4. Conclusions

The structure of radial 1D van der Waals heterostructures consisting of carbon nanotubes wrapped by BN and MoS_2 nanotubes was examined by numerous techniques such as absorption, transmission, reflection, ellipsometry, Raman spectroscopy, XPS, and ultrafast THz and optical pump-probe spectroscopy. This complex improved understanding of the opto-electronic properties is important in the drive towards nanoelectronics 1D van der Waals heterostructures.

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References

1. Geim, A.; Grigorieva, I. Van der Waals heterostructures. *Nature* **2013**, *499*, 419–425.
2. Burdanova, M.G.; Liu, M.; Staniforth, M.; Zheng, Y.; Xiang, R.; Chiashi, S.; Anisimov, A.; Kauppinen, E.I.; Maruyama, S.; Lloyd-Hughes, J. Intertube Excitonic Coupling in Nanotube Van der Waals Heterostructures. *Adv. Funct. Mater.* **2021**, *32*, 2104969.
3. Burdanova, M.G.; Kashtiban, R.J.; Zheng, Y.; Xiang, R.; Chiashi, S.; Woolley, J.M.; Staniforth, M.; Sakamoto-Rablah, E.; Xie, X.; Broome, M.; et al. Ultrafast Optoelectronic Processes in 1D Radial van der Waals Heterostructures: Carbon, Boron Nitride, and MoS_2 Nanotubes with Coexisting Excitons and Highly Mobile Charges. *Nano Lett.* **2020**, *20*, 3560–3567.
4. MBurdanova, G.; Tsapenko, A.P.; Kharlamova, M.V.; Kauppinen, E.I.; Gorshunov, B.P.; Kono, J.; Lloyd-Hughes, J. A Review of the Terahertz Conductivity and Photoconductivity of Carbon Nanotubes and Heteronanotubes. *Adv. Optical Mater.* **2021**, *9*, 2101042.