

Ultrafast nonlinear absorption in SWNTs: an ultra-broadband investigation

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Abstract

Z-scan spectroscopy is used to reveal ultra-broadband nonlinear absorption across different orders of resonant transitions in single-wall carbon nanotube ensembles, demonstrating the potential of nanotubes for nonlinear optics beyond the conventional NIR range.

I. INTRODUCTION

Carbon nanotubes and graphene have emerged as capable nonlinear optical materials for a wide range of photonic and optoelectronic applications [1-6]. In particular, their wideband optical absorption has triggered a great deal of research activities in the area of mode-locked fiber and solid-state lasers, where they may provide advantages in terms of wideband spectral coverage, low-cost fabrication and simplicity of integration than current technologies based on semiconductor heterostructures. For single-wall carbon nanotubes (SWNTs), the absorption typically consists of a series of excitonic absorption bands arising from the van Hove singularities in the density of states (DOS) [7, 8]. While the low orders of near-infrared excitonic absorption bands, i.e. S11 and S22 of semiconducting SWNTs are routinely employed for laser mode-locking applications, the metallic-tube transitions and other high-order transitions in the UV-visible range have drawn negligible attentions thus far. Although there have been a few reports on wideband nonlinear absorption characterization of SWNTs, these are typically confined within the near-infrared absorption bands [3]. Knowledge of the broadband optical properties of the SWNTs transitions is still limited, and it will provide useful insights if all the different orders of transitions within the same SWNTs ensembles could be probed and compared.

II. EXPERIMENTAL RESULTS

Here, we fabricated SWNT-polymer composite films and studied its nonlinear optical absorption across all the relevant resonant peaks, including: the first and the second semiconducting excitonic transitions at ~ 1800 nm (S11) and 1000 nm (S22); the first metallic excitonic transitions at ~ 700 nm (M11) and high-order transitions at ~ 500 nm for the same ensemble of SWNTs. Pronounced saturable absorption is observed across the whole wavelength range, unambiguously establishing the nonlinear nature of different orders of high-energy transitions. A comparison of the strength of nonlinear

absorption between different transitions is also made. While the S11 and S22 transitions demonstrate better performance in terms of modulation depth and saturation intensity, the other transitions also exhibit pronounced saturable absorption behavior, similar to those observed in semiconducting tubes in non-resonant conditions. Our results provide direct experimental evidence that nanotube-based nonlinear optical devices have the potential to be extended from the conventional infrared wavelengths to UV and visible wavelengths.

We use commercially available arc-discharge SWNTs. ~ 50 μm free-standing SWNT-carboxymethyl cellulose polymer composites are fabricated using a solution processing method described in Ref [2, 3]. Fig. 1(a) shows the optical absorption spectrum of the SWNT-composite (black) and pure polymer (red). The mean tube diameter is ~ 1.5 nm, as evidenced from the absorption peak positions [8].

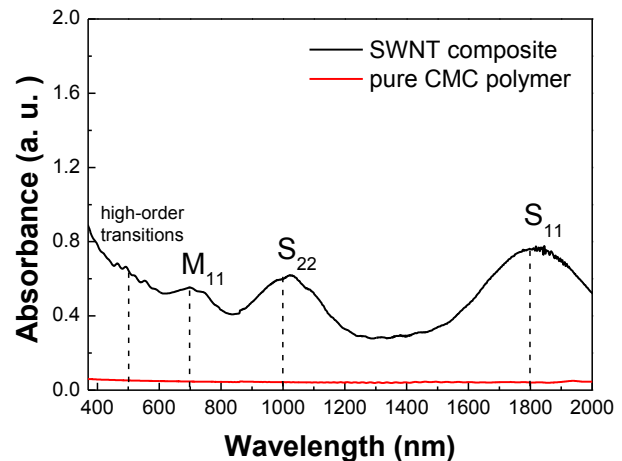


Fig.1 Absorption curve of the SWNT composite film.

Broadband tunable Z-scan experiment based on a Ti:Sapphire amplifier/OPA system (~ 100 fs, 1 kHz repetition rate) is carried out. We investigate the visible and near-infrared (500 nm - 1800 nm) spectral region. To avoid laser damage, we limit our excitation power to a range within which Z-scan curves are readily reproducible without any change in linear transmittance. Fig. 2(a-d) shows exemplary Z-scan data curves for excitation at 1800 nm (S11 band), 1000 nm (S22 band), 700 nm (M11 band), 500 nm (high-order transition band), respectively. At higher pump powers, all samples exhibit reverse saturable absorption, which confirms that real

saturable absorption, not photo-damage, is responsible for the enhanced transmission observed at the beam focus region. Pronounced saturable absorption is observed for all wavelengths investigated. The nonlinearity observed for high-order and the M11 transitions are shown in Fig. 2(a-b). Fig. 2(e) compares the normalized absorption for all the transitions for the same ensemble of SWNTs. The strongest nonlinearity is observed at the S11 resonance ~ 1000 nm. A modulation depth of $\sim 55\%$ and a saturation intensity of ~ 10 MW/cm² are obtained. The M11 band exhibits a modulation depth of $\sim 20\%$ and a saturation intensity of ~ 20 MW/cm². At the high-order transition wavelength, both modulation depth ($\sim 10\%$) and saturation intensity (~ 160 MW/cm²) degrade compared with those for the longer wavelength cases. However, the nonlinear absorption parameters are similar to those observed for semiconducting tubes in non-resonant conditions and is sufficient for laser mode-locking applications. It should be mentioned that as there is an overlap of density of states at the wavelength shorter than the S11 transition wavelength (1800 nm), the exact contributions from metallic and semiconducting tubes, to the observed saturable absorption, cannot be fully resolved at this stage. Further experiments in the non-resonant regions are currently underway to provide further clarification of the ultra-broadband nonlinear absorption.

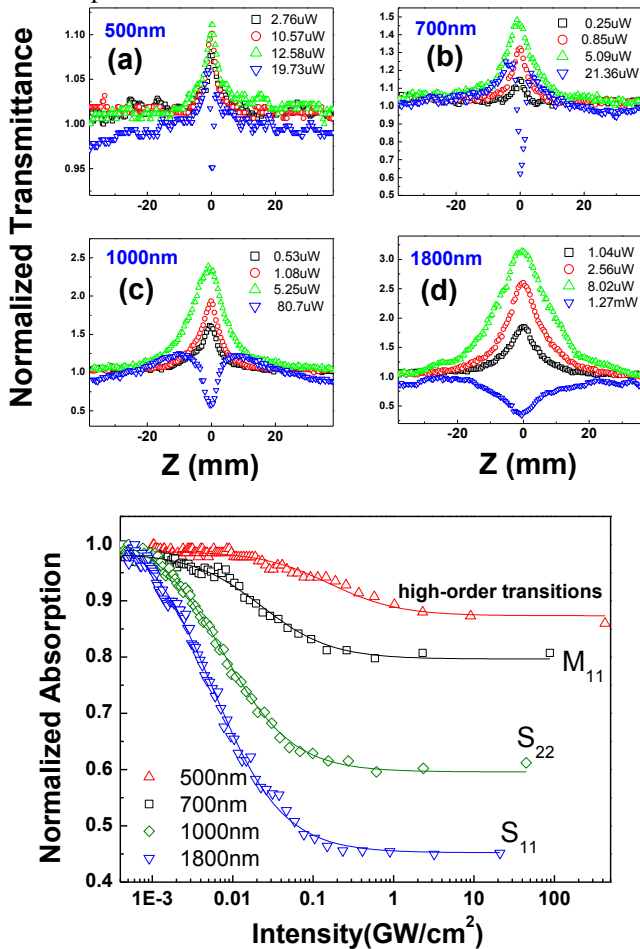


Fig.2 (a-d) Z-scan curves; (e) Normalized absorption with fittings (solid lines) for 1800nm, 1000 nm, 700 nm, 500 nm.

III. CONCLUSIONS

This work provides, to the best of our knowledge, the first direct experimental verification of strong optical nonlinearity of SWNT ensembles across visible to near-infrared (500 – 1800 nm), covering the relatively less explored metallic and high-order optical resonant transitions. The strength of nonlinear absorption across different spectral regions (S11, S22, M11 and higher-order transitions) is quantitatively compared for the same ensemble of nanotubes. The ultrafast nonlinearity exhibited by SWNTs in the higher energy transition bands may open up new opportunities for novel nonlinear photonic devices in the UV and visible range.

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