Carbon Nanotubes in a Photonic Metamaterial: Giant Ultrafast Nonlinearity through Plasmon-Exciton Coupling

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We demonstrate that a combination of carbon nanotubes with metamaterial offers a new paradigm for the development of a media with exceptionally strong ultrafast near-infrared nonlinear optical response which can be controlled by metamaterial design.

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We demonstrate exceptionally strong ultrafast optical nonlinearity by functionalizing photonic metamaterial with single-walled semiconductor carbon nanotubes. The nonlinearity is achieved through strong coupling between weakly radiating Fano-type resonant plasmonic modes of metamaterial and excitonic responses of carbon nanotubes. Following a "combinatorial" approach to material engineering we show that the appearance of an exceptionally strong ultrafast near-infrared optical nonlinearity can be tailored by appropriate metamaterial design.

Single walled semiconductor carbon nanotubes (CNTs) possess unique nonlinear optical properties as they exhibit high third-order susceptibility with sub-picosecond recovery time. Combining CNTs as nonlinearity agents with metamaterial structures provides the opportunity to link the plasmonic resonances of metamaterials with the excitonic resonances of nanotubes. In our experiments we used a planar structure that belongs to the class of metamaterials supporting dark mode plasmonic excitations [1]. In such metamaterials weak coupling of the excitation mode to the free-space radiation modes creates narrow reflection, transmission and absorption resonances with asymmetric, Fano-like dispersion. Here we used a structure complementary to the split ring wire metamaterial: a double periodic array of asymmetrically split ring slits in a metal film (see Fig. 1).

![Fig. 1. Two-dimensional nanoscale array of slits in a gold film forming the metamaterial structure (left). Metamaterial unit cell covered by CNTs, arrow pointing at a single nanotube crossing the slit (right).](QTuD5.pdf)

The metamaterial structures were fabricated by focused ion beam milling through a gold film evaporated on a Si₃N₄ membrane. On a single membrane we manufactured five metamaterial arrays with overall sizes 22 x 22 µm² and different unit cell size varying from to 731 nm to 839 nm. Spectral position of the plasmonic resonance of metamaterial depends on the unit cell size so we used combinatorial approach to study the linear and nonlinear response varying spectral separation of the main excitonic resonance of CNTs from the plasmonic resonance of the metamaterial. The Au@Si₃N₄ metamaterial structures were functionalized with single walled semiconductor carbon nanotubes with a characteristic diameter of 1.4 nm. Figure 1 shows helium ion microscope images of the metamaterial before and after functionalization with CNTs.

The nonlinear response of the metamaterial was investigated with a broadband ultrafast super-continuum fiber source equipped with a tunable 10 nm bandwidth spectral filter. The measurements were taken at a maximum fluence level of about 40 µJ/cm² corresponding to the average power level on the sample of only a few mW.
The spectra of the nonlinear response are presented on Fig. 2. The nonlinear response of the metamaterial has a complex frequency dispersion that could be decomposed on two main components derived from the analysis of the response in structures with different unit cell sizes. The first component that is practically independent of the unit cell size is relevant to the bleaching of the carbon nanotube excitonic resonance. Here increase of the light intensity leads to an increase of transmission. On Fig. 2b this component of the response is illustrated by a dashed bell-shaped line with amplitude $A_1$ that is centered at the CNT’s exciton absorption peak at 1950 nm. This bleaching response is superimposed to a much sharper “negative” peak of reduced transmission. The “negative” component is linked to the reduced damping of the plasmon mode through exciton-plasmon coupling. Here the nonlinear response may be compared with that of CNTs deposited on a bare $Si_3N_4$ membrane: one can see that the CNT’s response on the unstructured substrate (peak $A_3$) is about 12 times smaller than the overall “negative” response of the CNTs on the metamaterial (peak $A_2$). One can also argue that the positive response on the CNTs (peak $A_3$) is a factor of 13 smaller than that of the positive component of the CNT’s response in the metamaterial (peak $A_1$). The enhanced non-linear response of the composite metamaterial-carbon nanotube system is due to the resonant increase of the plasmon fields in the vicinity of the slits in the metal film through which light penetrates the metamaterial.

Importantly, the metamaterial environment allows to spectrally tailor the nonlinear response and even reverse the sign of optical nonlinearity. Indeed, the resonance nonlinear properties of the suggested composite metamaterial can be easily tuned throughout the near-IR by employing carbon nanotubes of different diameter and appropriately scaling the metamaterial. This makes carbon nanotube metamaterials very promising media for various nanophotonic applications, such as optical limiting and control of laser emission.

[1] V. A. Fedotov, M. Rose, S. L. Prosvirnin, N. Papasimakis and N. I. Zheludev, “Sharp Trapped-Mode Resonances in Planar Metamaterials with a Broken Structural Symmetry”, Phys. Rev. Lett. 99, 147401 (2007).