Investigating edge-functionalized graphene nanoribbons in the visible to NIR regime via scattering-type scanning near-field optical microscopy

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***Abstract*—Edge-functionalizing has been found to fine-tune the opto-electronic and magnetic properties of graphene nanoribbons (GNRs). In this work, we characterize perylene imide attached GNRs (PMI-GNRs) in the visible to NIR range via scattering-type near-field optical microscopy and discuss the possibilities of observing plasmon resonances within the same.**

Introduction

Plasmonics have found numerous applications in chemical detection, photovoltaics, nanoscale photometry, nonlinear optics etc. Controlling these collective excitations have been of prominent interest in recent years. The ultrahigh carrier mobilities of selected 2D materials, such as graphene, have made them candidates for tuneable plasmon excitations and biosensors with higher sensitivity than metallic ones have been realized [1].

Graphene nanoribbons (GNRs), which are graphene strips with widths up to a few 10s of nanometres, have garnered interest due to their interesting opto-electronic and magnetic properties. These are particularly interesting due to their non-zero band gap in comparison with graphene. GNR plasmons have greatly been explored in the mid-IR frequencies and although ways of pushing their plasma frequency towards the visible to NIR regime (e.g. via doping) have been theoretically predicted, to the best of our knowledge they have not yet been experimentally observed [2].

Edge functionalization of GNRs with functional groups such as anthraquinone (AQ), naphthalene imide (NMI) and perylene imide (PMI) have demonstrated the ability to fine tune the optoelectronic properties partly due to their supramolecular self-assembly[3]. The band gap in these functionalised GNRs hence has been demonstrated to lie in the visible range, with bandgap energies of ~2 eV. In this work, we investigate the plasmonic behaviour of these materials utilising scattering-type scanning near field optical microscopy (s-SNOM) in the visible and NIR range. We observe strong near-field amplitude and phase contrast as we move from visible to near infrared. As these properties relate to the dielectric function of the material (i.e. reflectivity and absorption), we calculate an approximate plasmon resonance frequency for varying edge functional groups and discuss the potential of increased absorption in this range due to plasmonic excitation. Achieving plasmonic resonances in visible-NIR ranges can have massive impacts on photonics and communication technologies.

Experimental details and results

A. Sample and experimental details

Edge-functionalized ribbons, PMI-GNRs were synthesized as per the previously reported procedure[3]. Briefly, polyphenylene precursor bearing one bromo group and one dodecyl chain per repeating unit was obtained through the AB-type Diels Alder polymerization of tetraphenylcyclopentadienone-based monomer. Bromo group on the precursor polymer was substituted with perylene monoimide through Suzuki coupling reaction to yield PMI functionalized polymer. The PMI polymer was subsequently converted into PMI-GNR through the oxidative cyclo-dehydrogenation using $FeCl_3$ in dichloromethane and nitromethane. Purified PMI-GNRs were dispersed into 1,2,4-trichlorobenzene and dilute solutions were drop casted on freshly peeled graphite surface to form self-assembled structures of straight and uniform nanoribbons[3], as shown in fig. 1.

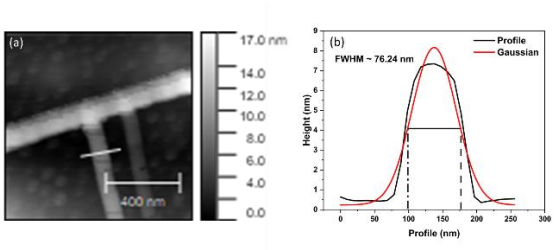

Fig. 1: (a) AFM image of PMI-GNR bundles. (b) Line profile across one bundle

The Vis-NIR s-SNOM in the CUSTOM facility at the University of Manchester consists of a Neaspec s-SNOM system integrated with 4 continuous wave lasers with wavelengths 633 nm, 785 nm, 1064 nm and 1550 nm. This is further coupled to the apex of an AFM tip, which is operated in tapping mode. The system works with a pseudo-heterodyne detection scheme enabling the extraction of the amplitude and phase independently of the scattered light. The scattered signal is demodulated at higher harmonics of tapping frequency of the tip to reduce far-field background noise and isolate the near field signal. By scanning the sample underneath the AFM tip in tapping mode, both the topography and the scattered near-field amplitude and phase can be mapped simultaneously.

B. Results

We observed a strong contrast in the near-field amplitude and phase images between sample and substrate as we move from 633 nm to 785 nm. But this decreased as we move onto 1550 nm, the contrasts are almost non-existent. As the phase of the near-field signal relates to absorption and the near-field amplitude relates to reflectivity, this suggests increased absorption around ~785nm. A quantitative estimate of these contrasts was obtained by obtaining a profile across the ribbon bundles and plotted against the wavelength as shown in fig. 2.

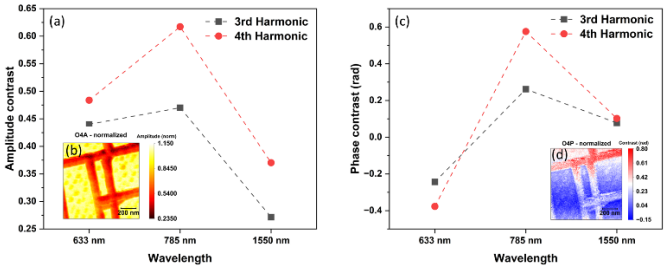

Fig. 2 : (a) & (c) Amplitude and phase contrasts for PMI-GNRs across wavelengths. Insets (b) and (d) shows the amplitude and phase images at 785 nm

A rough approximation of the plasmon resonance frequency for our nanoribbon sample was theoretically predicted using the formula,

$$\hbar\omega_{GSp} = \sqrt{\frac{4\alpha}{\epsilon_1 + \epsilon_2} E_F \hbar c q} \tag{1}$$

where E_F is the Fermi Energy (~ 1 eV), ħ is the reduced planck's constant, α is the fine structure constant given by 1/137, ω_{GSP} the plasmon resonance frequency, α is a constant given by 1/137, ϵ_1 (1) and ϵ_2 (2) are the dielectric constants at the two interfaces, c the speed of light and q the plasmon wavevector [45]. An excitation wavelength of approximately 890 nm was obtained for a ribbon width of 6 nm. This correlates with our experimental observations, as an increase in contrast is observed as we move towards 785 nm. We therefore expect this contrast to further increase up to ~890 nm, before reducing. In future studies, we will also investigate other NIR frequencies (e.g. 1 μm) beyond our calculated plasmon frequency to determine if we are observing a plasmon resonance in these materials.

Summary and future work

The opto-electronic behaviour of PMI-edge functionalized GNRs were characterized using s-SNOM in the visible to NIR regime. Strong amplitude and phase contrasts were observed at 633 nm and 785 nm, which almost vanished at a higher NIR wavelength. A theoretical approximation indicated the presence of plasmon resonance in the range considered. Future scope for this work would involve narrowband s-SNOM imaging of the sample near the predicted wavelength to visualize the plasmon polariton propagation in the ribbons. The exact fermi energy needs to be found out from conductivity measurements and hence the accuracy of the prediction can be improved.

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