RATIONAL BOTTOM-UP ASSEMBLY OF TAILORED MOLECULAR AGGREGATES ON NANOCARBON FOR HIGH SENSITIVITY NONLINEAR OPTICAL AND LIGHT HARVESTING APPLICATIONS

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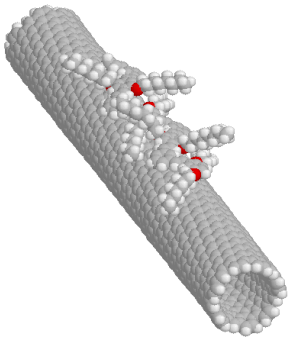
Nanocarbons, i.e. single-walled nanotube (SWNT) and graphene surfaces can mediate the self-assembly of polymers and large conjugated organic and organometallic, e.g. dye, molecules on their surfaces and thereby create organised molecular structures which would not form in solution or free space. Such aggregates, supramolecular assemblies of dye molecules, can possess sharp optical absorption bands and large optical cross sections so that they can photosensitise nanocarbon devices with high selectivity and sensitivity. In addition, these aggregates can modify the intrinsic electronic structure of the underlying nanocarbons locally and thereby generate locally defined electronic structures which are not available in neat nanocarbon particles. This is of particular relevance to emerging graphene electronics, which is one of the most promising technologies for going beyond current CMOS, as detailed in the 2010 update of the ITRS International Technology Roadmap for Semiconductors.



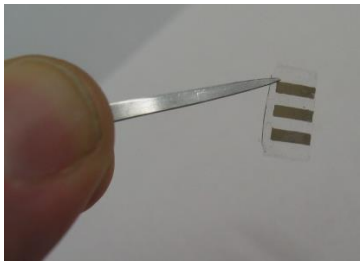
Dye aggregates are assembled on graphene sheets and nanotubes in dispersions and on thin films, in which we can exploit their extraordinary field effect mobility to detect optical absorption events. It is now possible to prepare defect-free, clean (down to atomic scale) nanotube and graphene devices [1]. Intimate interaction between dye molecules and atomically clean device surfaces enables aggregate assembly.

The following are fundamental scientific issues that can be addresses while developing dye aggregate-functionalized nanotube and graphene nonlinear optical and light harvesting devices:

- Structure of dye aggregates on nanotube and graphene surfaces.
- Impact of direct $\pi-\pi$ interaction between dye molecules and graphitic surfaces.
- Fundamental mechanism of photosensitisation of nanotubes and graphene sheets using tailored dye aggregates, as measured by ultrafast nonlinear optical and photoconduction responses.
- Fundamental mechanism of local modulation of nanotube and graphene electronic structure through aggregate electric fields and polymerised aggregate pressure.
- Impact of intense electric field near nanotube surface on dye aggregates with large linear and hyper-polarisability.

Photonic devices fabricated using nanoscale materials are essential building blocks in developing novel linear and nonlinear optical applications, especially light sources, photodetectors and solar cells.

- For nonlinear optical applications, the major challenge is to increase the optical absorption cross section of the material to enable large ultrafast response in the near-infrared. For graphene and carbon nanotube optical limiters, for instance, excessively high light intensity is required to induce a useful effect [2].
- For nanoscale photodetectors (and solar cells), the major challenge is to increase the optical absorption cross section of the material to enable detection at low light intensities. For carbon nanotube photodetectors, high light intensities of 1 kW/cm^2 are required to induce photoconductivity [3]. Such small sensitivities reduce their utility. Therefore there is a dire need to tailor and increase the sensitivity of the ultrafast nonlinear optical response as well as the efficiency of nanoscale light-harvesting.



Semiconducting carbon nanotubes exhibit significant nonlinear optical response [2] and can detect light as they are direct band gap materials [4]. However, for SWNTs produced using chemical vapour deposition, band gaps range approximately from 0.8-0.4 eV. No synthesis technique is available to produce nanotubes with mono-disperse diameters. Therefore, the characteristic optical absorption cut-off wavelengths vary from 1.4 to 2.8 μm without any control at the synthetic level. This renders any efforts to engineer the optical responses of nanotube-based sensors *futile*. However, polar dye aggregates on nanocarbon surfaces will modify the local electronic structure though a Stark effect and therefore generate locally modulated electrical and optical properties. Furthermore, if we can assemble polymerisable molecular aggregates on such surfaces, the bond length changes involved in the polymerisation process will apply a relatively large local pressure thereby modulating the local electronic structure. This process may be particularly interesting in converting semimetallic graphene particles to semiconducting ones.

[1] Ishigami, M, Chen JH, Cullen WG, Fuhrer MS, and Williams ED, Nano Letters, 2008, 7, p. 1643
[2] Wang J, Chen Y, Blau WJ, J Mater Chem, 2009, 19, p. 7425
[3] Freitag, M, Avouris PH et al., Nano Letters, 2003, 3, p. 1067
[4] Avouris, PH, Freitag M, and Perebeinos V, Nature Photonics, 2008, 2, p. 341