Chemical modification of graphene and carbon nanotubes: optical and electrical signatures of charge transfer doping and covalent functionalization

F. Lapointe[1], P. Lévesque[1], B. C. Saint-Antoine[2], S. Choubak[2], M. Biron[2], D. Bouilly[1], J. Guillemette[3], P. Desjardins[2], T. Szkopek[3] and R. Martel[12]

Regroupement Québécois sur les Matériaux de Pointe
[1] Département de chimie, Université de Montréal, Montréal, QC, H3C 3J7, Canada
[2] Département de génie physique, École Polytechnique de Montréal, Montréal, QC H3A 2A7, Canada
[3]Department of Electrical and Computer Engineering, McGill University, Montréal, H3A 2A7, Canada

The chemical functionalization and doping of the carbon lattice of graphene and carbon nanotubes are important processing steps aiming at building new functional interfaces for nanodevices. The attachment of adducts to the carbon sp^2 lattice affects however the material electronic and optical properties. Charge transfer doping by atmospheric gas for instance was found to control the overall properties in most carbon-based field-effect transistors (FETs) operating in air. This talk aims to provide an overview of the different issues related to the covalent functionalization and chemical doping of graphene and carbon nanotubes. We will present their respective signatures in the electrical, optical and thermoelectric properties of the layer and discuss on the different alternatives investigated so far to achieve a better control of the interface and device properties.

By using both carbon nanotube and exfoliated graphene layers as testbeds, we measured the influence of the chemical nature of the substrate and the impact of different gas exposure on the switching behaviour of both nanoscale and thin-film nanotube FETs. Our study revealed that electrochemical charge transfer doping by the water/oxygen redox couple is the underlying mechanism behind the environmental effects in most carbon-based transistors. [**1]** A solution to control the air doping using plastic substrates was found and the kinetics of the charge transfer process monitored using graphene FETs. [**2,3**] The doping mechanism is now understood using diagrams as presented in Figure 1.

The covalent functionalization of CVD graphene and carbon nanotubes was investigated using bromophenyl, methylene and hydrogen radical addition reactions. As an example, strong localization behaviors were observed in both SWNT **[4]** and graphene devices functionalized with monovalent chemical moisties. The optical signatures of doping and chemical functionalization of single-walled carbon nanotubes films with bromophenyl moisties was found in the mid-infrared (MIR) absorption spectra as asymmetric line shape of the phonon modes at ~870 and ~1600 cm^{-1}, which was ascribed to Fano resonance. [**5**] These signatures will be discussed in the context of device operation. Strategies that combine extensive functionalization with interesting optical and electrical conductivity will be presented.

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$$O_2(aq.) + 4H^+ + 4e^-(graphene) \underset{red}{\overset{ox}{\rightleftarrows}} 2H_2O$$

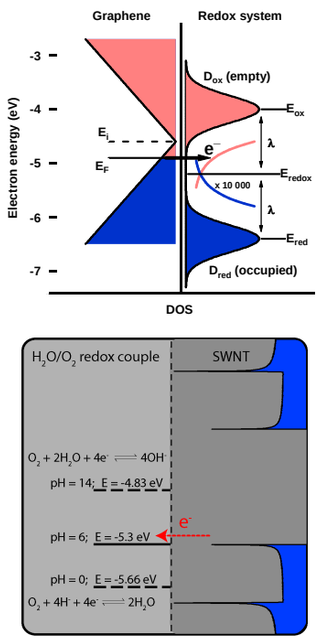

Figure. 1 Electron-transfer mechanism to grapheme and nanotubes. Top: Schematic of the water/oxygen redox couple density of states (DOS) and a comparison with the graphene DOS (top). The alignment of the redox potential with the SWNT DOS is also shown (bottom). The arrow indicates the direction of the charge transfer reaction.