Abstract

Poor understanding of the interactions at graphene/DNA interfaces has brought tremendous limitations to the development of label-free DNA-graphene based electrochemical/electrical biosensors. The aim of this study was to develop a label-free DNA/graphene-based electrochemical DNA hybridisation sensor, evaluate and benchmark its output electronic signal as a function of the effect of DNA on graphene's electronic properties. In addition, the study sought to understand the effect of graphene on the nature of DNA. Herein, results of the investigation of the effects of DNA self-immobilisation and subsequent DNA hybridisation on the electronic structure of CVD-grown graphene using a combination of Raman spectroscopy and conductance measurements are presented. A novel UV-Vis spectroscopy dependent measurement technique for the label-free study of the interaction between DNA-graphene interfaces during DNA hybridisation on graphene is reported. Also presented in this work, is a new method of representing electronic events and DNA conformational changes during DNA detection on graphene from current-voltage measurements. Non-covalent assembly was used to immobilise single-stranded (ssDNA) probes on CVD-grown graphene. On CVD-grown graphene, Raman peak frequency shifts, intensities and widths of the G and 2D bands after adsorption of the ssDNA probe and its hybridisation with complementary and mismatched ssDNA strands were analysed. The effect of graphene on the structural and conformational changes of DNA upon hybridisation of the ssDNA on the graphene surface both before and after hybridisation with complementary and triple-base mismatch DNA targets were investigated by monitoring UV-Vis absorption peaks at the 200 nm to 300 nm range. The findings were further confirmed through XRD analysis. Using Riemann approximation method, the rate at which the energy is transformed (power) was computed from the area under current-voltage curves.

Significant sequence-specific features in Raman peaks of graphene upon self-immobilisation of ssDNA and subsequent hybridisation with complementary and mismatched target strands were observed. The shifts in G and 2D peak positions indicate a donor-acceptor interaction between ssDNA and graphene and charge transfer effects on graphene upon hybridisation. While n-type doping (red shift of the G peak) was observed during hybridisation with complementary strands, p-type doping (blue shift of the G peak) was observed for mismatched strands. These features can serve as fingerprints for the identification of the electronic structure of graphene that uniquely evolves during DNA immobilisation and DNA hybridisation. These findings demonstrate that Raman spectroscopy can be sufficiently used to fingerprint differences between graphene and samples of graphene coated with biological adsorbates and clusters such as DNA.

Hyperchromic and hypochromic effects were related to structural and conformational changes of DNA on graphene. An increase and a decrease in absorption for hybridisation with a complementary and triple-base mismatch target was observed, respectively (Wilk' Lambda = 0.172, F (3,636) = 1020, p =0.000 < 0.05). Differences in structure between perfectly complementary DNA duplexes and those that contain mismatches were also seen by complexities between 2θ = 11° to around 2θ =25° that appeared only in the XRD pattern of ssDNA-coated graphene when hybridised with a triple-base mismatch. Bathochromic and hypsochromic shift in absorption wavelengths confirmed DNA adsorption and desorption on graphene. Adsorption of ssDNA probe on graphene shifted the maximum absorption wavelength to longer wavelengths (bathochromic shift) and shifted to shorter wavelengths (hypsochromic shift) during desorption of DNA upon hybridisation of ssDNA coated-graphene with a complementary and triple-base mismatch. DNA Adsorption and desorption on graphene was further confirmed by the shift of kα1 and kα2 to lower angles in the XRD patterns. The effects of graphene on the chromophoric

structure of DNA was evident through the re-appearance of the signature DNA absorbance wavelength peak at 260 nm in the absence of graphene in solution. Findings of the study provide an alternative application of hyperchromic and hypochromic effects when concerning the illumination of interactions between DNA and graphene. Furthermore, it is proposed that by monitoring the absorbance wavelength and absorption intensity changes of DNA on the graphene surface (before and after hybridisation), interactions in DNA-graphene interfaces could be clarified and the influence of graphene on the conformational changes that occur to the DNA can be better understood. Therefore, the findings of this study shed more light on the understanding of DNA-graphene interfaces and can be instrumental to the design and fabrication of improved devices with consistent output signals.

The power obtained through the method presented in this work represents the electronic charge transfer events and conformational changes in DNA structure holistically. Two distinct electronic circuit configurations, parallel and series, were studied. Using this simple integrative approach of geometric interpretation of current-voltage measurements, a consistent general trend in DNA hybridisation on graphene was obtained, a trend that has not been established using Dirac point's back gate (V_g) values in this work and previous work reported in literature. It was observed that in both parallel and series configuration; hybridisation of the ssDNA coated graphene with a complementary DNA target results in a decrease in Power. When the ssDNA coated graphene was hybridised with triple-base mismatched strands, an increase in power was observed for both parallel and series configurations. This offers a consistent output electronic signal that deciphers selective and specific DNA hybridisation characteristics on graphene.