Abstract

The potential of graphene, graphite and amorphous carbon as DNA sensor platforms was investigated. Therefore, different functionalization strategies to bind DNA strands to graphene, thin graphite and amorphous carbon were tested. Furthermore, ultrathin graphite flakes were electronically characterized as a first step in the development of sp² carbon based sensors with electronic readout.

The hydrogen-terminated edges and defect sites of CNW, upstanding microplates made out of 4-6 stacked graphene sheets, were successfully functionalized with single stranded DNA. DNA strands were covalently bonded using a fatty acid linker molecule. The fatty acid linker was attached to the CNW edges through a photochemical reaction. This was followed by the EDC-mediated coupling of amino-labeled DNA to the carboxylic acid groups of the fatty acid linker. Hybridization experiments in combination with fluorescence microscopy allowed for the clear differentiation between fully complementary target DNA and DNA with a single mismatch, out of a 29 nucleotides sequence. The optimal hybridization temperature to achieve high selectivity was found to be 60 °C. Furthermore, hybridized DNA could be denatured and rehybridized for at least 10 cycles.

In order to increase the DNA functionalization levels, different functionalization routes that act upon the basal plane of sp² carbon were tested. First, a non-covalent method, based on π-π stacking, was investigated. A pyrene-like molecule was used to π-stack with the aromatic structure of graphene and graphite. The pyrene-like molecule also contained a carboxylic acid group that was used to couple DNA with the known EDC-mediated reaction. However, different experiments using fluorescence microscopy, fluorescence spectroscopy and XPS could not prove the binding of DNA or the pyrene-like linker to the graphene or graphite surface. The functionalizing species are probably rinsed off by mild washing steps.

A second, covalent, method was tested to functionalize the graphene and graphite surface with DNA strands. This method was based upon diazonium
The aim was to use the diazonium as a linker to attach the DNA, again via the known EDC-mediated reaction. Two different diazonium molecules were used. The first one resulted in nitro groups as an anchor point for further DNA coupling. Since the required reduction of the nitro groups into amino groups posed some problems, another diazonium molecule, with a carboxylic acid group, was used to facilitate the DNA coupling. This second type of diazonium, 4-benzoic acid diazonium tetrafluoroborate, was homemade by two different methods. Functionalization was investigated with Raman spectroscopy, as this method allows to characterize preselected individual flakes. The results from Raman spectroscopy (and XPS) indicated that a part of the diazonium physisorbs to the graphene, as it could be removed by thorough washing steps, while another part of the diazonium covalently binds to the graphene surface. This covalent binding was shown by the appearance of a defect-related D peak in the Raman spectra of functionalized samples. The presence of DNA was not clearly detected by the Raman spectroscopy and no real difference between EDC-positive and EDC-negative reference samples could be observed.

In addition to graphene-like materials, amorphous carbon microstructures were tested for their potential use in DNA sensing. The amorphous carbon microstructures contained an outer layer of nanostructured carbon, drastically enhancing the surface area. The amorphous carbon microstructures were successfully functionalized by the fatty acid route and by the diazonium route, as shown by confocal fluorescence microscopy. Bulk amorphous carbon microstructures, lacking the nanostructured outer layer, were used as a reference. It was clear that these bulk microstructures showed greatly reduced functionalization levels due to the much smaller surface area. The electrical resistance over bridge-shaped amorphous carbon microstructures was measured using a four probe technique. The resistance change for positive samples was 40 % lower than the change for EDC-negative samples, and this for the samples functionalized via the fatty acid route. Samples functionalized via the diazonium route display a difference in resistance change of 12 %. Bulk amorphous carbon structures did not show a difference in resistance change between positive and EDC-negative reference samples.

In order to further investigate the potential of sp² carbon as DNA sensor platforms, ultrathin graphite flakes were electronically characterized. Four
electrical contacts in van der Pauw configuration were deposited on individual flakes, with a thickness of 25 – 50 nm, using e-beam lithography. The samples showed a zero-field resistivity of 40 – 55 $\mu\Omega$ cm at room temperature. The magnetoresistance effect of the samples was studied in magnetic fields up to 2.06 T and in a temperature range of 5 K – 400 K. At fields of 2.06 T, positive magnetoresistance effects of up to 130 % and 235 % were found for temperatures of 300 K and 77 K respectively. It was also proven that in-plane components of the magnetic field had no effect on the magnetoresistance. Next, the Hall voltage was investigated in function of magnetic field (0.1 T – 2.06 T) and temperature (77 K – 400 K). The Hall voltage exhibits a linear field dependence for the lowest fields and shows a downward bent for higher fields. The charge carrier concentrations and mobilities were determined, using the zero-field resistivity and Hall measurements, for low magnetic fields in a temperature range of 77 K – 300 K. Charge carrier mobilities up to 891 cm$^2$/Vs ($n = 1.75 \times 10^{20}$ cm$^{-3}$) and 1329 cm$^2$/Vs ($n = 8.28 \times 10^{19}$ cm$^{-3}$) were found at 300 K and 77 K respectively.