

Non-covalent functionalisation of graphene using self-assembled monolayers

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Graphene, monolayer sheets of sp^2 -bonded carbon atoms arranged in a honeycomb-like structure, continues to attract intense research interest due to its unique electronic properties and potential applications. As a “surface-only” nanomaterial, the properties of monolayer or few-layer graphene structures are extremely sensitive to adsorbed ambient contaminants, with a correspondingly severe impact on the electrical characteristics and stability of graphene-based devices. Development of strategies for functionalisation of graphene without adversely affecting its electronic properties are of key importance. Here we report on a simple, versatile functionalisation method based on solution-phase formation of alkane-amine self-assembled monolayers (SAMs) on graphene; see Figure 1a for a schematic.

Ab initio calculations (2nd order Møller–Plesset perturbation theory), applied to a cluster model (methylamine on pyrene) yield a binding energy, $E_b = -220$ meV for the anchor amine group, when the amine is located above a C-C bond (an “over-bond” site). Similar values were found for calculations with the amine group located over a carbon atom (“over-atom” site, $E_b = -223$ meV) and for the amine located over the centre of one of the phenyl rings (“over-ring” site, $E_b = -215$ meV), indicating that there is no strong preferential bonding site to the graphene plane. The results are consistent with a non-covalent amine-graphene interaction (~220 meV binding energy), which is strong enough to enable formation of a stable aminodecane monolayer at room temperature ($T = 300$ K, $E_b \sim 8$ kT), but also sufficiently labile to allow the necessary mobility of the molecules required for formation of a close-packed monolayer. Atomistic molecular dynamics simulations for 784 1-aminodecane molecules on a 13 nm x 15 nm graphene substrate (not shown) predict formation of a mobile but stable alkane-amine SAM, with nearest-neighbour distances for the amine anchor groups ~ 0.33 nm.

Measured Raman spectroscopy data for graphene monolayers deposited on thermally oxidised silicon substrates and then functionalized with 1,10-diaminodecane (red data in Fig. 1b) are also consistent with a non-covalent, charge-transfer interaction between the alkane-amine molecules and graphene. The presence of a sharp two-phonon 2D peak (full-width at half-maximum intensity, $FWHM \sim 24.5$ cm^{-1}), a characteristic of monolayer graphene, and the absence of a defect (D) peak close to 1350 cm^{-1} following functionalization (Fig. 1b, inset) confirms that the layer of 1,10-diaminodecane molecules does not perturb the sp^2 -hybridisation of the graphene monolayer and does not introduce additional structural defects. Further, the spectrum for the functionalised monolayer shows several significant differences when compared with data measured for an as-deposited graphene monolayer (Fig. 1b, gray data). Both the shift in the G peak position towards higher energy and the reduction in intensity of the 2D peak following functionalisation of the exposed graphene surface with 1,10-diaminodecane are consistent with doping, likely via charge transfer from the amine anchor groups to the graphene.

Figure 1c shows two-probe resistance (R_{2P}) vs gate voltage (V_g) data measured in vacuum for a monolayer graphene field-effect device following fabrication. The data show the expected behaviour for unpassivated graphene devices exposed to ambient conditions – hysteretic ambipolar conduction, with minimum conductivity (Dirac Point, $V_{g,DP}$) at positive gate voltage. This positive value of $V_{g,DP}$ indicates unintentional hole doping, likely from contaminants at the graphene surface and the graphene-substrate interface, e.g., adsorbed water and organic residue from the fabrication process. Figure 1d shows the R_{2P} - V_g data for the same device, acquired following *ex situ* annealing to 250 °C under nitrogen for 1 hour, functionalisation in solution with 1-aminodecane and transfer under ambient conditions (~ 1 hour) to the vacuum measurement chamber. Several significant changes are evident, including a shift in the Dirac Point to negative gate voltage and a sharper resistance peak (higher carrier mobility) around the Dirac Point for each sweep. These negative values for $V_{g,DP}$ in the functionalised device indicate adsorbate-induced electron doping, presumably from the amine anchor groups in the 1-aminodecane molecular layer. Kim et al. have proposed a simple device model to interpret two-probe R_{2P} - V_g data²⁵. Using three fit parameters — the contact resistance (R_c), the impurity carrier density (n_0) and the field-effect mobility (μ_{FE}) — the two-probe device resistance can be expressed as

$$R_{2P}(V_g) = R_C(V_g) + \frac{L}{We\mu_{FE}\sqrt{n_0^2 + [n(V_g, V_{g,DP})]^2}} \quad (1)$$

where L ($\approx 6 \mu\text{m}$) and W ($\approx 10 \mu\text{m}$) are the device length and width, respectively, e is the electronic charge and n is the gate-induced carrier density, $n \propto |V_g - V_{g,DP}|$ if quantum capacitance effects are excluded. The inset to Fig. 1d shows fits to Equation 1 for the data in the main panel, yielding estimates for both the mobility, $\mu_{FE} \approx 2350\text{--}2500 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$, and the impurity carrier density, $n_0 \approx 0.8 \times 10^{12} \text{ cm}^{-2}$, assuming a constant contact resistance $R_C = 200 \Omega$ for both sweeps. In general, devices functionalised with 1-aminodecane following annealing show higher carrier mobilities and also improved stability upon re-exposure to ambient conditions compared with annealed “bare” devices, suggesting that the 1-aminodecane layer can act as a barrier to hinder the readsorption of contaminants, e.g., water.

A key challenge in the development of graphene-based nanoelectronics is the deposition of inorganic dielectrics onto graphene for top-gated devices. “Seeding” processes for atomic layer deposition (ALD) of inorganic dielectrics onto graphene have been reported, including ozone pre-treatment, and also deposition of thin ($\sim 10 \text{ nm}$) polymer layers containing appropriate binding groups. Use of self-assembled monolayers represents an attractive complementary process. The smaller thickness of the alkane-amine SAM, compared to polymer layers, would increase the effective total dielectric capacitance, and the defect density in SAM-modified graphene should be lower than for ozone-treated graphene. Figure 1e shows a scanning electron microscopy image of an ultra-thin film of aluminium oxide (5 nm nominal thickness), which was deposited onto highly-oriented pyrolytic graphite that had been functionalised with 1,10-diaminodecane. Uniform coverage of the substrate (including some small defects and a step edge) is evident. Figure 1f shows the edge of the aluminium oxide film following removal of part of the film using adhesive tape. The remaining aluminium oxide shows good adhesion to the substrate. The film is quasi-continuous film arising from coalescence of two-dimensional islands, as expected for the chosen film thickness.

In conclusion, self-assembled monolayers of alkane-amines represent a versatile new route for non-covalent functionalisation of graphene without adversely affecting its unique properties. Advantages for nanoelectronic applications include adsorbate doping, surface passivation and seeded ALD. Selection of suitable terminal groups for binding of target species onto graphene opens up possibilities for selective and sensitive graphene-based electromechanical or electrochemical (bio)sensors. This work was supported by the European Commission under the FP7 ICT project “GRAND” (215572).

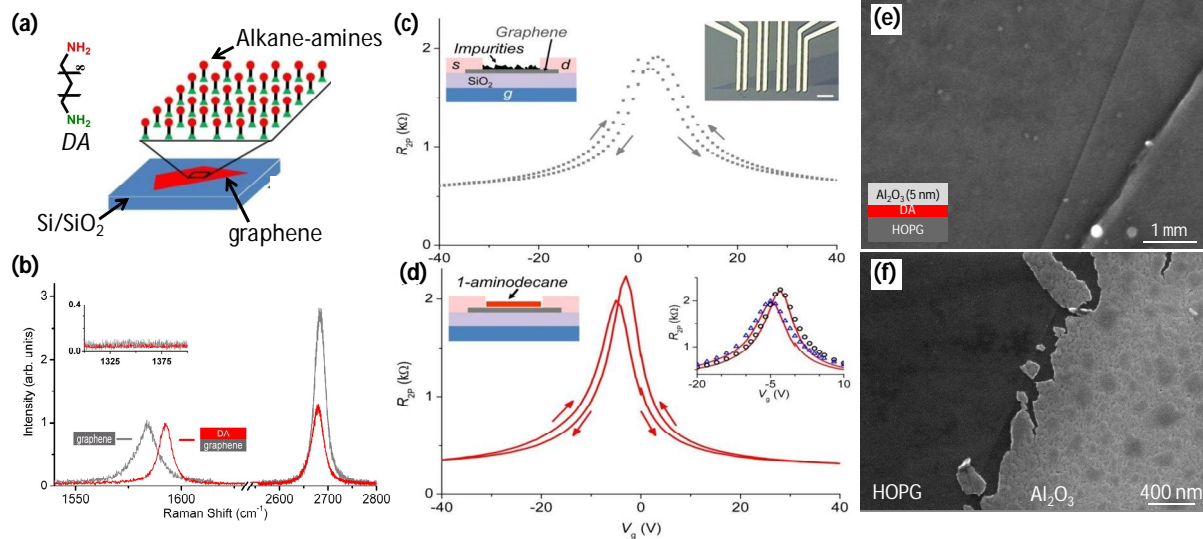


Figure 1 (a) Left: Structure of 1,10-diaminodecane (DA). Right: Schematic of a graphene layer functionalised with a monolayer of alkane amines. (b) Raman spectra (514.5 nm excitation) for a graphene monolayer deposited onto an unmodified Si/SiO₂ substrate (gray) and also for a graphene monolayer (red) following functionalisation in solution with 1,10-diaminodecane (DA). Inset: No defect (D) peak $\sim 1350 \text{ cm}^{-1}$ is observed following functionalisation. (c) Two-probe resistance vs. gate-voltage ($R_{2P}\text{--}V_g$) characteristics measured in vacuum for a back-gated, monolayer graphene device following fabrication. (d) $R_{2P}\text{--}V_g$ characteristics for the same device measured following *ex situ* thermal annealing under nitrogen (200 C) and functionalisation in solution with 1-aminodecane. Fits to the $R_{2P}\text{--}V_g$ data for the functionalised device (d, inset) yield estimates for the device mobility, $\mu_{FE} \approx 2350\text{--}2500 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$. (e) SEM image of a conformal 5 nm thick Al₂O₃ film deposited using atomic layer deposition onto a graphite substrate, which had been functionalised with 1,10-diaminodecane. (f) SEM image of the edge of the Al₂O₃ film and the underlying graphite (HOPG) substrate following removal of part of the Al₂O₃ film using adhesive tape.