

Non-covalent functionalization of graphene with a hydrophilic self-limiting monolayer for macro-molecule immobilization



Concha Bosch-Navarro^{a,b,*}, Zachary P.L. Laker^a, Alexander J. Marsden^a, Neil R. Wilson^a, Jonathan P. Rourke^b

^a Department of Physics, University of Warwick, Coventry CV4 7AL, UK

^b Department of Chemistry, University of Warwick, Coventry CV4 7AL, UK

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ABSTRACT

Two different pyrene-substituted ions were used to render the surface of graphene hydrophilic. Self-limiting monolayers of ammonium and sulfonate substituted pyrenes were used to give, respectively, an overall positive and negative charge to the surface. Both pyrenes gave a stable hydrophilic surface and were used to selectively immobilise negatively or positively charged macro-molecules. This simple and versatile non-covalent approach can be used on graphene on a variety of substrates (e.g. copper, SiO₂), suspended graphene, and also for graphite.

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Introduction

Graphene displays a remarkable combination of properties: it has high thermal conductivity and high charge carrier mobility, it is almost optically transparent, and is strong, stiff and flexible [1]. This has led to many proposed applications, including in sensing [2–4] and catalysis [5,6]. However, its simple and robust structure also leads to some difficulties: like graphite, it is hydrophobic and its smooth van der Waals surface does not lend itself to selective adsorption of biomaterials [7,8]. This makes sensors based on pristine graphene unselective in their response, and leads to compatibility issues for aqueous processing routes. Hence, for many applications, controlling graphene's surface functionality becomes essential. This necessitates chemical modification which should be done in such a way so as to retain the beneficial physical properties of graphene and in as thin a modified layer as possible so as to maximise the contribution of graphene to the hybrid material. Even low-level covalent functionalisation rapidly degrades the electronic properties of graphene [9–11], so non-covalent functionalisation which retains the sp² graphene structure is preferred.

Molecules with planar delocalised π systems are often chosen for non-covalent functionalisation of graphene [11], as these can interact with the extended electronic system of the graphene surface by van der Waals or electrostatic interactions, commonly

referred to as π stacking [12]. To this end, layers of small molecules on graphene such as perylenebisimides [13–15], phthalocyanines [16,17] or pyrenes (pyr) [18–22] have been investigated. Pyr derivatives are particularly interesting as their chemical versatility has been widely exploited to create carbon-based hybrid materials through π stacking [23–27], and to assist the exfoliation of graphite to graphene [28–31]. Hence, they provide an easy and flexible route to modifying the surface properties of graphene. Here we design pyrene derivatives to form self-limiting monolayer films on graphene in order to make the surface positively or negatively charged in solution. This turns the graphene from hydrophobic to hydrophilic and enables controlled macro-molecule adsorption through electrostatic interactions.

Results and discussion

We designed pyrene derivatives that would non-covalently bind to the Gr surface, but would remain non-reactive. Thus, we attached non-coordinating charged moieties via a flexible linker to a pyrene core, as shown in Fig. 1. The pyr-carrying ammonium cation (trimethyl-(2-oxo-2-pyren-1-yl-ethyl)-ammonium bromide; pyr⁺) [32] and pyr-carrying sulfonate anion (sodium (2-oxo-2-pyren-1-yl-ethyl)-sulfonate; pyr⁻) were synthesized (for details see S11). During deposition from solution, the hydrophobic π -conjugated pyrene core should bind strongly to the Gr surface by π stacking, whilst electrostatic repulsion between the charged moieties should self-limit the film to monolayer coverage.

* Corresponding author.

E-mail address: concepcion.bosch@uv.es (C. Bosch-Navarro).

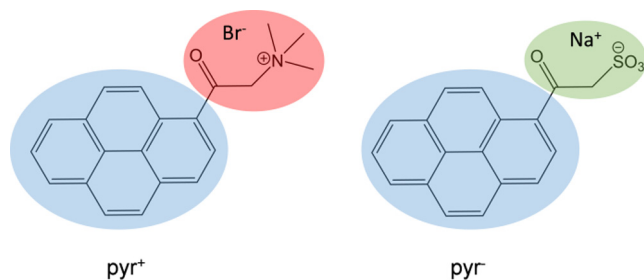


Fig. 1. Representation of trimethyl-(2-oxo-2-pyren-1-yl-ethyl)-ammonium bromide (pyr^+) and sodium (2-oxo-2-pyren-1-yl-ethyl)-sulfonate (pyr^-). The molecules consist of a hydrophobic part (highlighted in blue) designed to adhere to the surface of graphene through π - π forces, and a charged moiety (highlighted in red and green) that then controls the surface functionality.

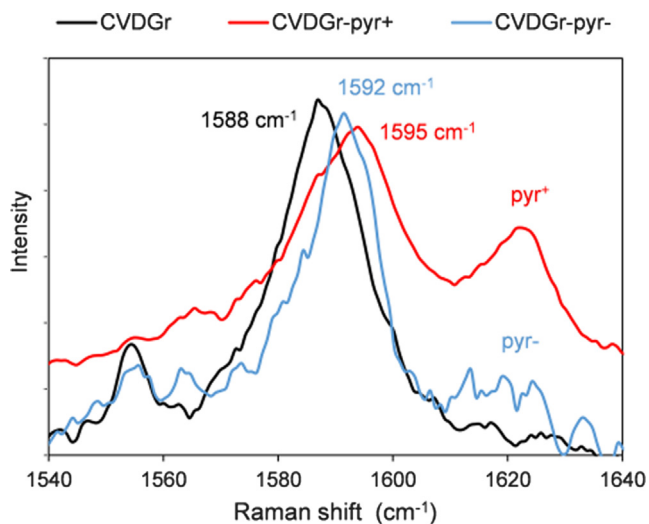


Fig. 2. Raman spectra of CVDGr (black), CVDGr- pyr^+ (red) and CVDGr- pyr^- (blue). The spectra were acquired with an excitation line of 633 nm.

To test this, the pyr-derivatives were deposited on chemical vapour deposition (CVD) grown graphene on copper. This is an ideal substrate for studying molecular deposition on graphene [13,17]: it is of technological relevance and presents a clean, flat and well defined surface for detailed studies. Large area monolayer graphene was synthesized by CVD on copper foil using methane as the precursor (for details see methods and [Supplementary Infor-](#)

[mation Section 1, SI1](#)) and its uniformity and quality were confirmed by scanning electron microscopy and Raman spectroscopy (SI2-SI3). As-produced graphene-on-copper (CVDGr) samples were immersed overnight in ethanolic solutions containing the pyr^+ molecule, or methanolic solutions containing the pyr^- molecule. After drying, Raman spectroscopy confirmed the presence of the pyrene derivatives on the CVDGr, with a new band corresponding to the pyr moieties appearing at around 1620 cm^{-1} as shown in Fig. 2 (see also SI3). Moreover, the graphene G band upshifts by $4\text{--}7\text{ cm}^{-1}$ (from 1588 cm^{-1} in CVDGr to 1592 cm^{-1} in CVDGr- pyr^+ and to 1595 cm^{-1} in CVDGr- pyr^-), indicative of electrostatic doping of Gr by the charged moieties after functionalization [20,33–35]. X-ray photoelectron spectroscopy (XPS) further confirmed the presence of pyr^+ and pyr^- , and proved that only a very thin layer of modified pyr was deposited on the CVDGr, consistent with a monolayer coverage (see SI4). Atomic force microscopy (AFM) analysis showed that the deposited layers of pyr^+ and pyr^- on CVDGr were thin and homogeneous. Topography images (Fig. 3a and SI6 for CVDGr- pyr^+ and CVDGr- pyr^- , respectively) after surface modification are almost indistinguishable from CVDGr, showing the facets that form on the copper substrate after graphene growth [36] and with no obvious pyr agglomerates. The presence of the pyr^+ / pyr^- films is revealed by selectively removing small regions by first scanning in contact mode (controllably scratching away the molecular layer) and then scanning a larger region in tapping mode and hence scanning across covered and uncovered areas (Fig. 3b). AFM height profiles (Fig. 3c and SI6) indicate the presence of a thin molecular layer on the Gr of about 0.2 nm for both CVDGr- pyr^+ and CVDGr- pyr^- , observable due to the locally smooth graphene on copper surface [37], again consistent with monolayer coverage. We note that by contrast similar depositions of unmodified pyrene on CVDGr appeared to form three dimensional islands rather than uniform monolayers (SI7). Scanning tunnelling microscopy (STM) investigations under ambient conditions were unfortunately unable to resolve the molecular packing. Ab initio calculations have shown that pyr stably adsorbs flat to graphene, and that the binding energy increases when electron donating or withdrawing groups are substituted to the pyr [38]. Hence, although previous reports have found that pyrene can desorb in solution [21], with electropolymerisation a possible approach to stabilising them [22], here we found the modified pyrene layers to be stable. However, at room temperature the pyr are expected to move rapidly along the graphene surface and hence would not be easily visible by STM.

Static contact angle measurements (SCA) were performed to examine the wetting properties of CVDGr before and after non-

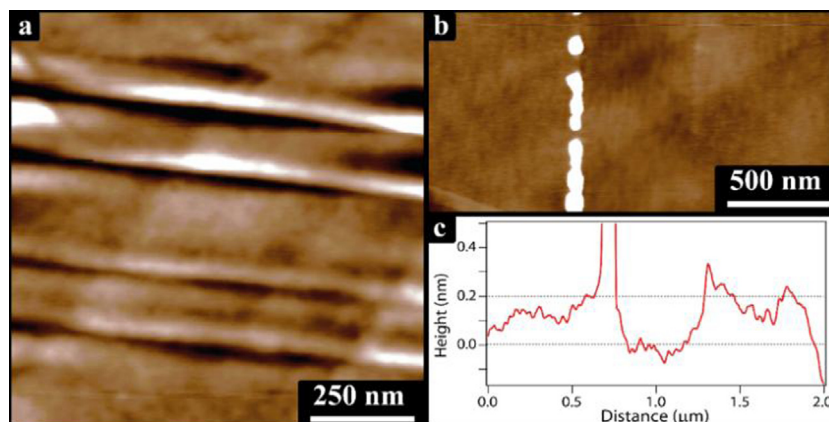


Fig. 3. a) AFM topography image of CVDGr- pyr^+ . b) AFM topography image showing the scratch over CVDGr- pyr^+ created by employing AFM in contact mode, root mean square roughness excluding the scratch is 0.3 nm . c) Height profile corresponding to (b), consistent with the presence of a monolayer of pyr^+ over CVDGr. The full height scales of the AFM images are 5 nm .

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