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Reversible Switching of the Dirac Point in Graphene Field-Effect Transistors Functionalized with Responsive Polymer Brushes

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ABSTRACT

The reversible control of the graphene Dirac point using external chemical stimuli is of major interest in the development of advanced electronic devices such as sensors and smart logic gates. Here, we report the coupling of chemo-responsive polymer brushes to reduced graphene oxide (rGO) based field-effect transistors (FETs) to modulate the graphene Dirac point in the presence of specific divalent cations. Poly[2-(methacryloyloxy)ethyl]phosphate (PMEP) brushes were grown on the transistor channel by atom transfer radical polymerization (ATRP) initiated from amine-pyrene linkers non-covalently attached to rGO surfaces. Our results show an increase in the Dirac point voltage, due to electrostatic gating effects, upon the specific binding of Ca^{2+} and Mg^{2+} to the PMEP brushes. We demonstrate that the electrostatic gating is reversibly controlled by the charge density of the polymer brushes, which depends on the divalent cation concentration. Moreover, a theoretical formalism based on the Grahame equation and a Langmuir-type binding isotherm is presented to obtain the PMEP-cation association constant from the experimental data.

INTRODUCTION

Graphene, a two-dimensional semiconducting material, is one of the most promising materials for post-silicon electronics due to its outstanding physical and electronic properties.¹⁻³ Due to its great sensitivity, graphene can be used as the chemo-to-electrical signal transducing material in field-effect transistors (FETs) for the generation of high-performance responsive devices, such as advanced sensors and smart logic gates.⁴⁻⁷ For these applications, the reversible modulation of the graphene electronic properties (i.e., the doping level) by a specific external (bio)chemical stimulus represents a key feature.^{8,9} The chemo-electrical signal transduction in graphene FETs is based on various mechanisms, including charge transfer, charge scattering, capacitive effect and electrostatic field-effect.¹⁰ Among them, the electrostatic field-effect (also referred as electrostatic gating) is widely regarded as the most reliable sensing mechanism,¹¹ and consists of the modulation of the Fermi level by means of an external electric field, for example, the local electric field induced by the adsorption of charged macromolecules.^{12,13} The modulation of the Fermi level by electrostatic gating is observed as a shift in the Dirac point voltage.

To confer specificity to the transducer, recognition elements need to be anchored on the graphene surface. For instance, the use of monoclonal antibodies or enzymes as recognition elements has led to FET sensors with a low limits of detection and high sensitivity.¹⁴⁻¹⁷ Unfortunately, the biomolecule activity is affected by changes in temperature, pH, ionic strength as well as the presence of inhibitors. Furthermore, an irreversible denaturation of the biomolecule structure with a complete loss of its functional activity can occur in harsh conditions.¹⁸ This issue is an important limitation for the development of FET devices for sensing applications.¹⁹ To solve this problem, synthetic and robust "recognition elements" anchored on the transducer surface should be used.

Regarding the electrostatic gating sensing mechanism, the synthetic receptors have to display controllable charge density as a function of a specific target concentration and be located directly onto graphene. In this sense, chemo-responsive polyelectrolytes seem to be an ideal "recognition element" because they display high charge density that controllable via chemical means.^{20,21} Hence, the use of polymer brushes^{22,23} is an attractive alternative to generate synthetic and robust responsive interfaces²⁴⁻³¹ for FET sensing devices.³²⁻³⁵

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2 As an example, Hess et al. reported the covalent functionalization of graphene with polymer brushes
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4 containing weak cation monomer units (N,N-dimethylaminoethyl methacrylate, DMAEMA). Due to the
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6 polymer brushes nature, the pH sensing range of the graphene FETs has been modified enhancing the
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8 enzymatic detection of acetylcholine.³⁵ Since graphene FETs present the inherent property of sensing pH
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10 changes,³⁶ the DMAEMA monomer units do not confer to the graphene FETs a new recognition function, but
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12 they act as an enhancer of one already presented. Therefore, it is still a challenging task the use of stimuli-
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14 responsive polyelectrolytes to confer to the graphene interface a new selective interaction. In this regard,
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16 polymer brushes containing phosphate monomer units turn out to be a promising system to be studied
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18 because on the one hand, they present high charge density and on the other hand, they can form strong
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20 complexes with some divalent cations (e.g., Ca^{2+} and Mg^{2+}).^{37,38}
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25 In this work, we report the polymerization of poly [2-(methacryloyloxy) ethyl phosphate] (PMEP) brushes on
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27 reduced graphene oxide (rGO) FETs to confer them a cation selective response (Ca^{2+} and Mg^{2+}). The growth
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29 of responsive PMEP polymer brushes was accomplished via surface-initiated atom transfer radical
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31 polymerization (SI-ATRP), a powerful approach to tune/adapt the chemical and physical properties of
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33 surfaces.^{39–41} Surface modification with PMEP brushes was characterized by X-ray photoelectron
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35 spectroscopy (XPS), ellipsometry, atomic force-microscopy (AFM) and contact angle goniometry. Then, the
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37 field-effect properties of the PMEP modified graphene transistors, in particular the Dirac point voltage, were
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39 studied in the presence of different types of cations. Finally, a theoretical formalism was introduced in order
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41 to obtain the PMEP-cation association constant from the experimental values of the Dirac point voltage at
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43 different Ca^{2+} concentrations. Our results show a strong influence of the PMEP brushes on the rGO FETs
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45 response provided that the presence divalent ions Ca^{2+} and Mg^{2+} promote significant changes in the Dirac
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47 point of graphene. We believe that these results further broaden the scope of action of polymer brushes to
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49 emerging technological areas, namely, graphene-based field-effect transistors.
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54 EXPERIMENTAL SECTION

55 **Materials**

1 Interdigitated microelectrodes (ED-IDA1-Au), as well as an electrochemical batch cell, were obtained from
2 Micrux Technologies (Oviedo, Spain). A concentrated graphene oxide solution was kindly supplied by the
3
4 Prof. Josef Breu's Laboratory (University of Bayreuth, Germany). Anhydrous N,N-dimethylformamide
5
6 (99.8%), hydrazine monohydrate (99%), (3-aminopropyl)-triethoxysilane (97%), 1-amine pyrene (97%), α -
7
8 bromoisobutyryl bromide (98%), triethylamine (99%), 2,2'-bipyridyl (99%), CuBr₂ (99.999%) and 2-
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10 (methacryloyloxy) ethyl phosphate (90%), referred to as MEP, were purchased from Sigma-Aldrich. THF (PA)
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12 was purchased from Anedra SA. This solvent was dried by refluxing in the presence of sodium (Aldrich, 99.8%)
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14 and benzophenone (Aldrich, 99%) until the observation of purple coloration and then distilled.
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20 **Graphene-based transistor fabrication**

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23 The reduced graphene oxide field-effect transistors (rGO FETs) were prepared from interdigitated electrodes
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25 as we described in previous works.^{16,42}
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28 **Poly [2-(methacryloyloxy) ethyl phosphate] (PMEP) brush growth on the transistor channel**

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31 PMEP brushes were obtained by surface-initiated atom transfer radical polymerization (SI-ATRP) on initiator-
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33 modified rGO-FETs. The functionalization involved three synthetic steps: 1) non-covalent functionalization of
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35 graphene surface with amine-pyrene, 2) acylation of amine-pyrene groups with α -bromoisobutyryl bromide
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37 to prepare the surface-confined ATRP initiator and, 3) ATRP polymerization of 2-(methacryloyloxy) ethyl
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39 phosphate (MEP).
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43 *1) rGO-FETs modification with amine-pyrene:* the rGO-FETs chips were incubated in 2 mM amine-pyrene
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45 solution prepared in a dimethylformamide (DMF) for 4 h, rinsed with DMF and Milli-Q water and finally dried
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47 with N₂.
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50 *2) Acylation of amine modified rGO-FETs with α -bromoisobutyryl bromide to obtain ATRP initiators sites:*⁴³

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52 The amine modified rGO-FETs substrates were immersed in an Erlenmeyer containing 40 mL of dry THF and
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54 2 mL of triethylamine under N₂. After this, the reaction solution was placed in an ice bath and 2 mL of α -
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56 bromoisobutyryl bromide was added slowly using a pressure-equalizing dropping funnel. After 3 h, the
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58 transistors were removed and washed with acetone, ethanol and Milli-Q water.
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2 3) *Growth of PMEP brushes from immobilized initiators*: The ATRP polymerization was carried out according
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4 to the method described by Zhou et al.⁴⁴ 12.5 g of MEP was dissolved in 20 mL of water and neutralized with
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6 NaOH solution to produce the di-sodium salt. Then, 0.4 g of 2,2'-bipyridyl and 0.011 g of CuBr₂ was added
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8 and the solution was degassed by N₂ bubbling for an hour. Then 0.144 g of CuBr was added and the mixture
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10 was left for 15 min under N₂. Simultaneously, ATRP initiator modified rGO-FETs were sealed in Schlenk tubes
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12 and degassed through vacuum/N₂ cycles. Then, the reaction mixture was syringed into these Schlenk tubes,
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14 adding enough to cover the samples completely. The mixture was left overnight under N₂ at 60°C and then,
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16 the substrates were removed and washed with deionized water and dried with N₂.
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23 **Field-effect transistors characterization**

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25 Liquid-gated graphene FETs were measured using the batch cell from Micrux Technologies. Electrical
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27 measurements were performed by applying a 100 mV source-drain bias and sweeping the gate potential (V_g)
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29 while monitoring the current between the drain and the source (I_{ds}) using a Teq4 bipotentiostat (nanoTeq,
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31 Buenos Aires, Argentina). An Ag/AgCl reference electrode from BASi (Indiana, USA) was used as a gate
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33 electrode.
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36 **X-ray photoelectron spectroscopy (XPS)**

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38 An SPECS SAGE HR 100 XPS spectrometer was used. A Mg K α (1253.6 eV) X-ray source was employed
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40 operating at 12.5 kV and 10 mA. Quantitative analysis of spectra was carried out by using the Casa XPS
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42 software, employing Shirley baselines and Gaussian\Lorentzian functions. Surface-charging effects were
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44 corrected by setting the binding energy of the main component of the C1s core level at 284.6 eV.
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50 **Contact angle goniometry**

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52 A Ramé–Hart contact angle system (Model 290) at 25 °C and using 1 μ L drops. The average contact angle
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54 value was obtained at three different locations of the same sample.
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58 **Atomic force microscopy (AFM)**

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1 A Veeco Multimode AFM connected to a Nanoscope V controller was used to image the polymer brushes.
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4 AFM measurements were performed in tapping mode with a sample scan size of 2.5 $\mu\text{m} \times 2.5 \mu\text{m}$. Non-
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6 conductive sharpened silicon nitride probe (Bruker, $K = 0.12 \text{ Nm}^{-1}$) were used.
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8 9 **Ellipsometry**

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11 For the PMP film thickness estimation, an alpha-SE ellipsometer from Woollam Co. Inc. was used. The
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13 ellipsometric measurements were conducted using a wavelength range from 550 to 900 nm, an angle of
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15 incidence of 70° and the high-precision mode. A multilayer model taking into account the layers of different
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17 materials (i.e., APTES, rGO, aminepyrene and PMP) was used. All the layers were treated as Cauchy materials
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19 having the following wavelength-dependent refractive index: $n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$, where A, B, and C are fitting
20
21 coefficients and λ is the wavelength. To obtain the A, B and C coefficients for each layer, ellipsometric
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23 measurements were performed after each modification step and fitted with the CompleteEASE software.
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28 29 **RESULTS AND DISCUSSION**

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32 A set of interdigitated gold electrodes as source and drain electrodes, connected via a very narrow channel
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34 (10 μm) of rGO, was used for the preparation of the transistors (Figure 1a). The interdigitated arrangement,
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36 together with the liquid gate configuration, leads to FETs with an extremely high transconductance and a
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38 charge carrier mobility of 30 and 15 $\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for holes and electrons respectively, as described in previous
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40 works.^{16,42} Since the covalent attachment of molecules on graphene disrupts the π -conjugation structure,⁴⁵⁻
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a polymerization method which does not alter the semiconducting properties of the graphene needs to be
chosen. It has been shown that the self-assembly of aromatic compounds on graphene surfaces via π - π
stacking has no deleterious effects on the exceptional electronic quality of this material.⁴⁸ With this in mind,
we propose a SI-ATRP approach initiated from an amine-pyrene linker previously assembled to the rGO
surface (Figure 1b).

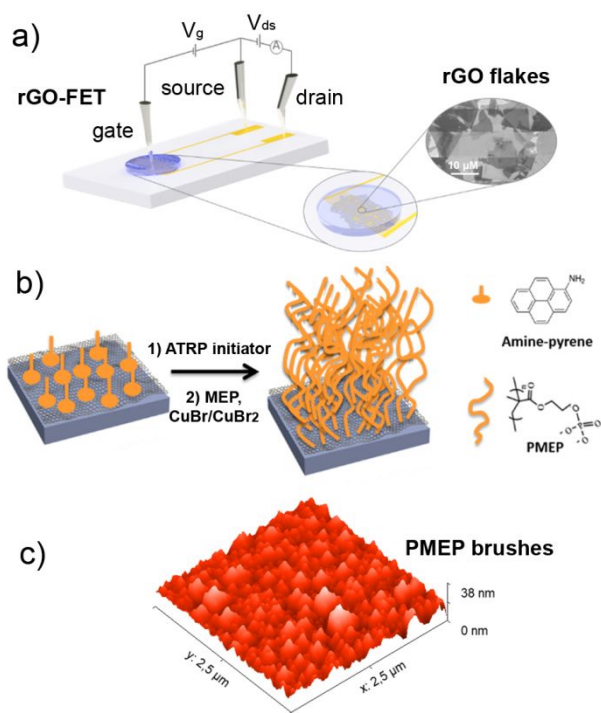


Figure 1. a) Illustration of the liquid gated rGO FET, the interdigitated source and drain electrodes and a SEM image of the rGO functionalized channel. b) Scheme of the rGO FET functionalization with PMEP brushes by atom-transfer radical-polymerization (ATRP). (c) Topography image of PMEP brushes obtained by atomic force microscopy (AFM).

The surface functionalization was characterized using X-ray photoelectron spectroscopy (XPS). The first two spectra in the Fig. 2a show the successful reduction of GO to rGO using hydrazine, as the intensity of the C-O peak decreases, in the presence of signals corresponding to other functional groups on the rGO surface. After the PMEP modification, the signal corresponding to O-C=O groups increased, which is consistent with the additional ester groups of the PMEP. Further, the effective functionalization of the rGO surface by PMEP is evidenced by the presence of the P 2s and P 2p XPS signals (Figure 2b). In another experiment, Ca and P spectra were recorded after the incubation of a PMEP modified rGO in 1 mM CaCl₂ and subsequent rinsing with deionized water to remove the salt excess. The resulting Ca/P ratio was shown to be 0.4 (Figure 2c) instead of 1. We attribute this observation to two plausible effects: (i) the presence of counterion gradients within the film, or (ii) the coexistence of mono- and dibasic phosphate species, instead of the sole presence of dibasic species, in the brush layer. Surface modification was also proved by contact angle measurements (see Fig. S1 in the SI file). Further, the PMEP thickness was studied by ellipsometry (Fig. S2) showing a film thickness of 19 ± 3 nm. This value is agreement with the thickness of PMEP brushes polymerized on gold and

silicon wafer using also the ATRP approach.⁴⁴ The AFM topography image of a rGO substrate modified with PMEP (Fig. 1c) reveals a continuous and uniform film with a roughness (in terms of the root mean square height) of 3.3 nm (additional scanning electron microscopy characterization is included in the SI file - Fig. S3).

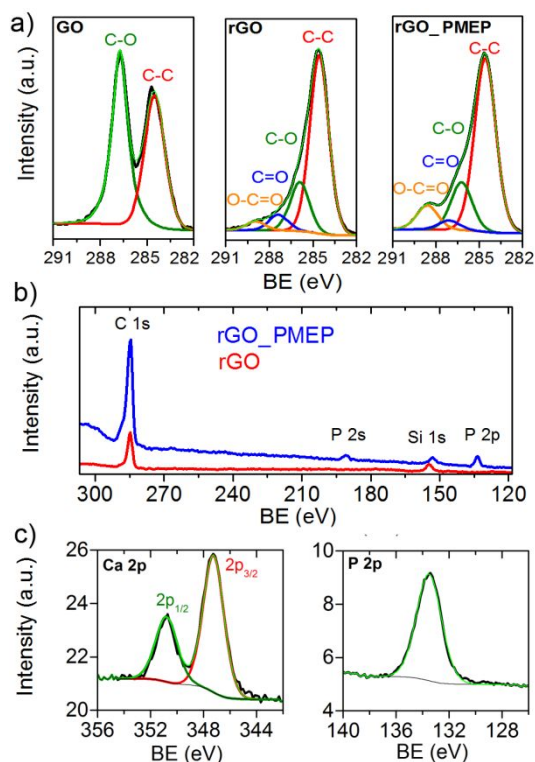


Figure 2. a) XPS spectra in the C1s binding energy region for graphene oxide (GO), reduced graphene oxide (rGO) and rGO functionalized with a PMEP brushes (rGO_PMEP) b) Comparison of the survey XPS spectra of rGO (red) and PMEP functionalized rGO (blue). c) Ca2p (left) and P2p (right) energy regions of rGO_PMEP after incubation in Ca²⁺.

To assess the chemo-responsive properties of the PMEP brushes, the contact angle was measured with solutions containing monovalent (K⁺) or divalent cations (Ca²⁺). Figure 3a shows contact angles of PMEP brushes prior to and after coordination with Ca²⁺. A marked increase in hydrophobicity was observed in the presence of the divalent cation, which is a result of a surface charge density decrease due to the PMEP coordination with Ca²⁺ ions.³⁸

Sweeping the gate potential (V_g) while monitoring the current between the drain and the source (I_{ds}) results in transfer characteristics with a minimum conductance corresponding to the minimum concentration of charge carriers (the so-called Dirac point). The left and right branches from this charge neutrality point

1
2 represent the hole and electron conductivity regimes, respectively.⁴⁹ We should note that after the MEP
3 polymerization a slight decrease in the FET transconductance was observed (Fig. S4) which could be
4 attributed to desorption of the rGO sheets not so strongly attached to the substrate surface. The negative
5 charge of the PMEP brushes induces an electric field that generates positive charges in the graphene channel
6 (i.e., holes into the valence band) and shifts the Fermi level below the Dirac point (Figure 3b). When Ca²⁺ ions
7 bind to the phosphate groups in the polymer brushes, the surface charge is neutralized and the transfer
8 characteristics shifts to more negative gate values. This phenomenon can be observed by comparing the
9 transfer characteristics in the presence and in the absence of Ca²⁺ (Fig. 3c). For the PMEP-modified FET, the
10 Dirac point (V_i) clearly shifts to more negative values upon binding of the divalent cations (right), whereas no
11 signal is observed in the control measurement using non-modified rGO FETs (left).

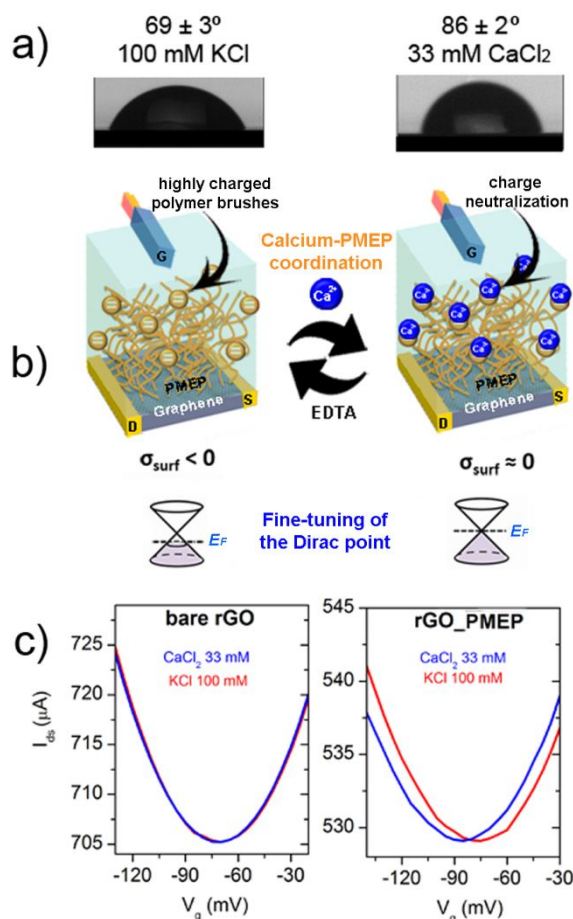
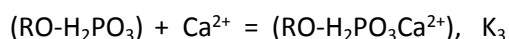
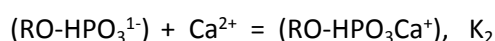
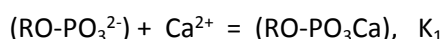


Figure 3. a) Contact angle of rGO surfaces modified with PMEP brushes and measured with solutions containing monovalent and divalent cations: 100 mM KCl (left) and 33 mM CaCl₂ (right). The values of the salt concentrations were chosen to keep the electrostatic screening length constant. b) Scheme of the PMEP brushes and the Fermi level before and after the binding of Ca²⁺ ions. c) Transfer characteristics for bare rGO FET (left) and rGO FET functionalized with PMEP (right) in the presence of 100 mM KCl (red) and 33 mM CaCl₂ (blue).

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4 Figure 4a shows that the binding of the analyte to the polymer brushes can be reversed by complexing the
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6 Ca^{2+} ions using 10 mM EDTA for 20 min. This treatment regenerates the negative charge of the brush and
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8 shifts the Dirac point (left) and the contact angle (right) back to the dissociated PMEP values. On the other
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10 hand, in the case of Ca^{2+} binding, we have observed that the signal reaches a stable value after a one-minute
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12 exposure time. Measuring the Dirac point shift (ΔV_i) at different concentrations of Ca^{2+} gives a response curve
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14 with a Langmuir-like adsorption behavior, where the polymer brush reaches a binding saturation close to 10
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16 mM Ca^{2+} (Fig. 4b). According to the experimental data taken from the linear regime, the sensitivity of the
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18 PMEP-modified FET device is 17 mV per decade. For sake of comparison, current Ca^{2+} sensors employing
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20 more sophisticated sensing configurations exhibit sensitivities close to 25 mV per decade. In principle, we
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22 assumed that all the monomer units are exposed to Ca^{2+} ions. In previous studies it has been demonstrated
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24 that in the case of thin polymer brushes (thickness < 100 nm) counterions fully penetrate the inner
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26 environment of the polymer layer.^{50–53} In our experiments, the thickness of the polymer brushes is ~ 20 nm;
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28 hence, we can infer that cations penetrate through the whole thickness of the macromolecular layer.
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33 A formalism based on the Langmuir-Freundlich binding isotherm and the Grahame equation was proposed
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35 to obtain the degree of PMEP coordination (i.e., the surface coverage) from the change in the Dirac point
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37 (ΔV_i). The modification of the graphene surface with very thin polymer brushes facilitates the use and
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39 application of this isotherm to describe the binding process. However, we recognize that above a critical
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41 thickness value this isotherm is no longer applicable and a more detailed analysis would be needed to
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43 describe the experiments.
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47 The binding equilibrium of Ca^{2+} to the phosphate groups of the polymer brushes can be described as follows:
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where parentheses are used to designate surface species and K_1 , K_2 and K_3 represent the respective equilibrium constants which are described in the Supporting Information file. As we worked at pH 10,⁵⁴ $[(RO-HPO_3^{-1})] \approx [(RO-H_2PO_3)] \approx 0$ and it is possible to assume that the divalent cation coordination is described by the K_1 equilibrium. Therefore, the PMEP-Ca surface coverage expression (θ) simplifies to:

$$\theta = \frac{(K_1[Ca^{2+}]_0)^m}{1 + (K_1[Ca^{2+}]_0)^m} \quad (1)$$

where $[Ca^{2+}]_0$ is the concentration of Ca^{2+} close to the PMEP brushes surface (see SI for $[Ca^{2+}]_0$ calculation) and m is called heterogeneity index. This adsorption model takes into account the heterogeneity of adsorption energy of the binding sites and the lateral ligand interactions, where m can take values ≤ 1 .⁵⁵

The surface charge density (σ) is a function of the concentration of phosphate charged groups and can be expressed as follows:

$$\sigma = 2e^- [(RO - PO_3^{2-})] \quad (2)$$

As phosphate groups are neutralized by the coordination to Ca^{2+} , the surface coverage can be written in terms of the surface charge density: $\theta = (\sigma_i - \sigma) / \sigma_i$, where σ_i is the surface charge density of a completely dissociated PMEP (i.e., in the absence of Ca^{2+}).

On the other hand, the Grahame equation relates the surface charge density to the electrostatic potential at the interface of the polymer brush (ψ_s):

$$\sigma = \sqrt{8\epsilon\epsilon_0 kT n_0} \sinh\left(\frac{e\psi_s}{2kT}\right) \quad (3)$$

The relation can be simplified for low ψ_s to $\sigma = \epsilon\epsilon_0 \psi_s / \lambda_D$, where λ_D is the Debye length. As de Dirac point (V_i) is proportional to the electrostatic potential,¹² the surface coverage can finally be expressed as follows:

$$\theta = \Delta V_i / \Delta V_{i, max} \quad (4)$$

where $\Delta V_{i, max}$ is the change of the Dirac point obtained upon saturation of Ca^{2+} .

The dependence of the surface coverage (calculated using equation 4) as a function of $[Ca^{2+}]_0$ was fitted with equation 1 to determine K_1 and m . Values corresponding to $K_1 = 301 \pm 42 \text{ M}^{-1}$ and $m = 1 \pm 0.2$ were obtained. These values are consistent with previously reported association constants of calcium with other (RO- PO_3^{2-}) molecules such as phosphatidylinositol (10 M^{-1}) and phosphatidylinositol 4,5-bisphosphate (500 M^{-1}).⁵⁶ Moreover, the value obtained for m evidence a very low degree of heterogeneity of the binding sites.

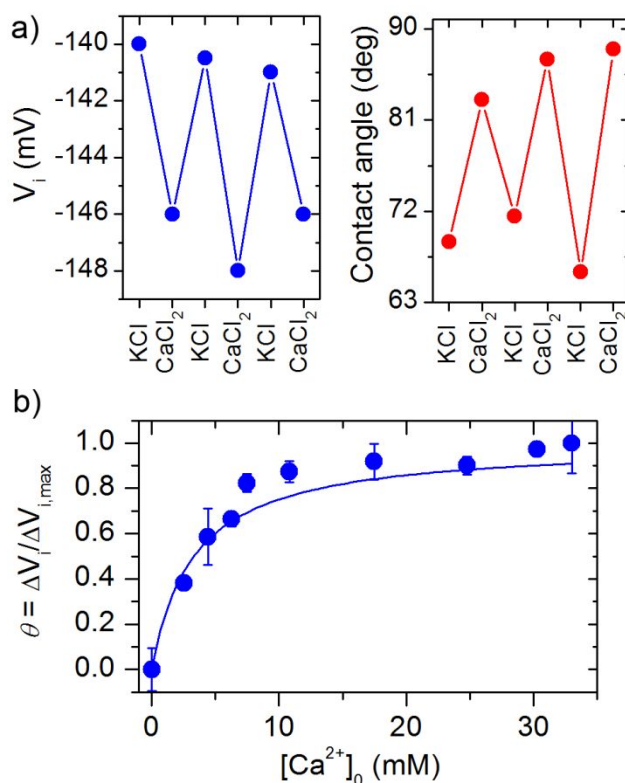


Figure 4. a) Reversibility of the Dirac point (left) and the contact angle (right) in the presence and the absence of Ca^{2+} . Between consecutive measurements the substrates were incubated in EDTA. b) Langmuir-Freundlich binding isotherm showing the surface coverage of PMEP coordinated by Ca^{2+} ions. The circles are the experimental results and the solid line is the fitting using the model described in the text.

It was also observed that the transconductance of the PMEP-modified rGO FET diminishes when Ca^{2+} binds to the polymer brush with respect to measurements in KCl (Fig. S5). This effect may be attributed to the collapse of the polymer brush upon binding of the divalent cation.^{4,38} A similar effect was observed for Mg^{2+} . The maximum Dirac point shift upon binding of Mg^{2+} ions was found to be of -2 mV (see SI for more details). This lower shift compared to the measurements performed with Ca^{2+} is expected since the affinity between phosphate and calcium is higher than the one corresponding to phosphate-magnesium.^{56,57}

CONCLUSIONS

In summary, an ion-responsive negatively charged polymer brush was grown on the graphene surface via atom transfer radical polymerization (ATRP) of poly[2-(methacryloyloxy)ethyl]phosphate (PMEP). The resulting chemo-responsive graphene-based transistor responds to the presence of the divalent ions Ca^{2+} and Mg^{2+} . Our results show a reversible modulation of the Dirac point voltage (by electrostatic gating effects) due to the divalent cation-PMEP coordination. The binding of Ca^{2+} showed a Langmuir-type binding behavior with an affinity constant of 301 M^{-1} . This functionalization approach, initiated from amine-pyrene linkers non-covalently attached to the rGO surface, represents a powerful tool to combine functional polymer brushes and rGO based FETs in order to develop chemo-responsive devices with responsive interfacial architectures. Since our polymerization approach could be extended to a wide variety of stimuli-responsive monomers, we believe that these results will have profound implications for the development of advanced sensors and smart logic gates.

ASSOCIATED CONTENT

Electronic supplementary information (ESI)

Scanning electron microscopy (SEM) images of PMEP modified rGO FETs, ellipsometric and transconductance measurements, and further PMEP characterization by contact angle are available.

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Notes

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11
12 CONICET.
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15 16 References

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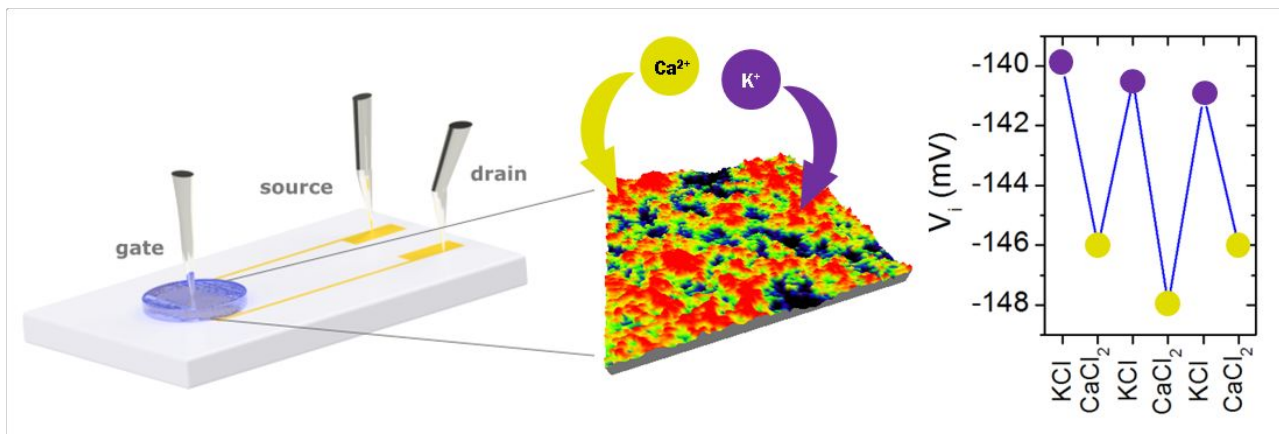
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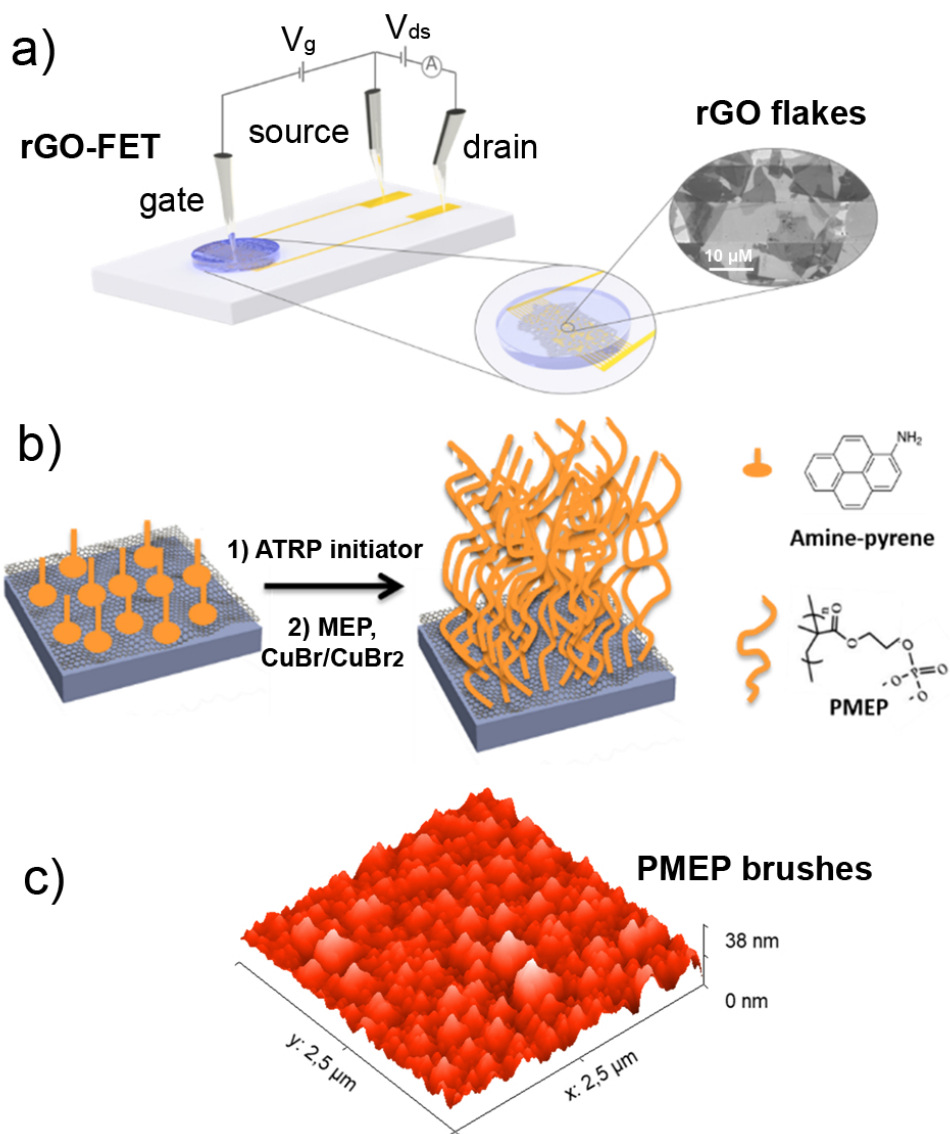
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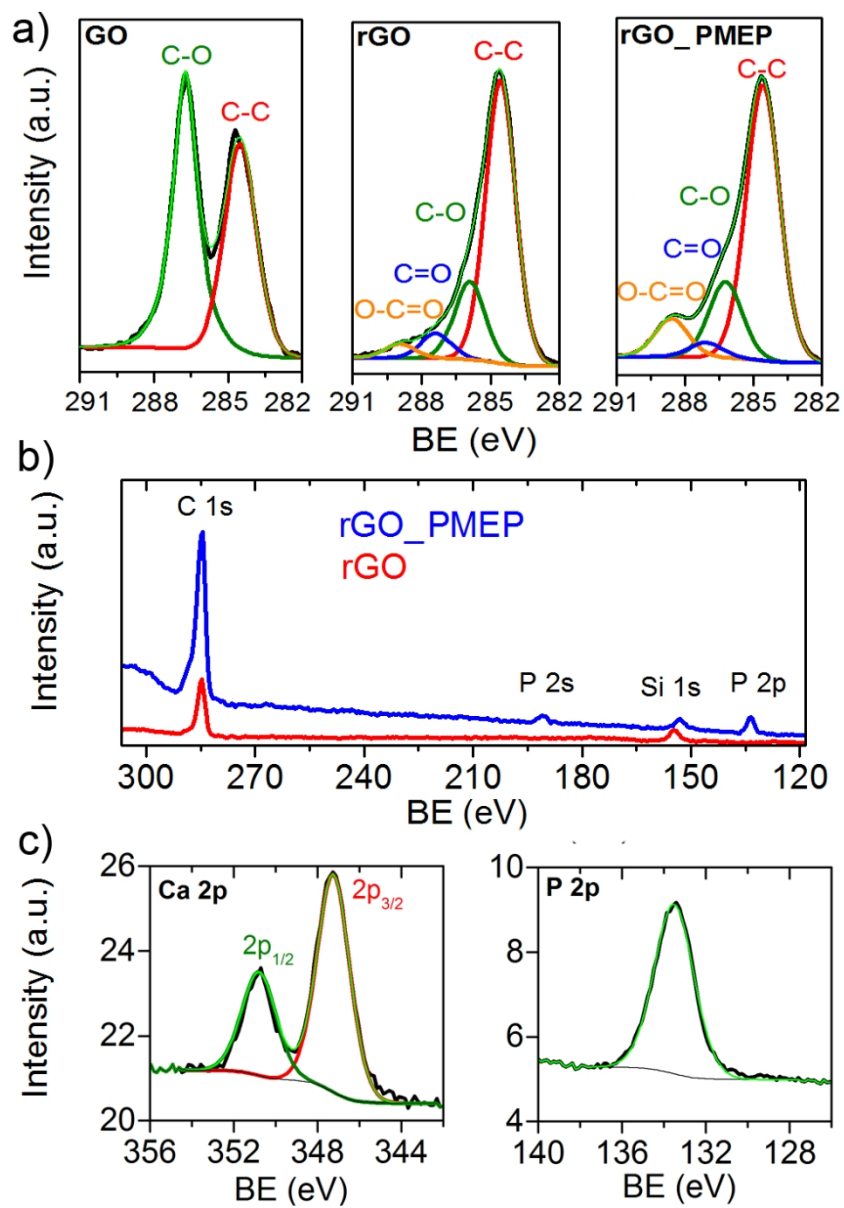
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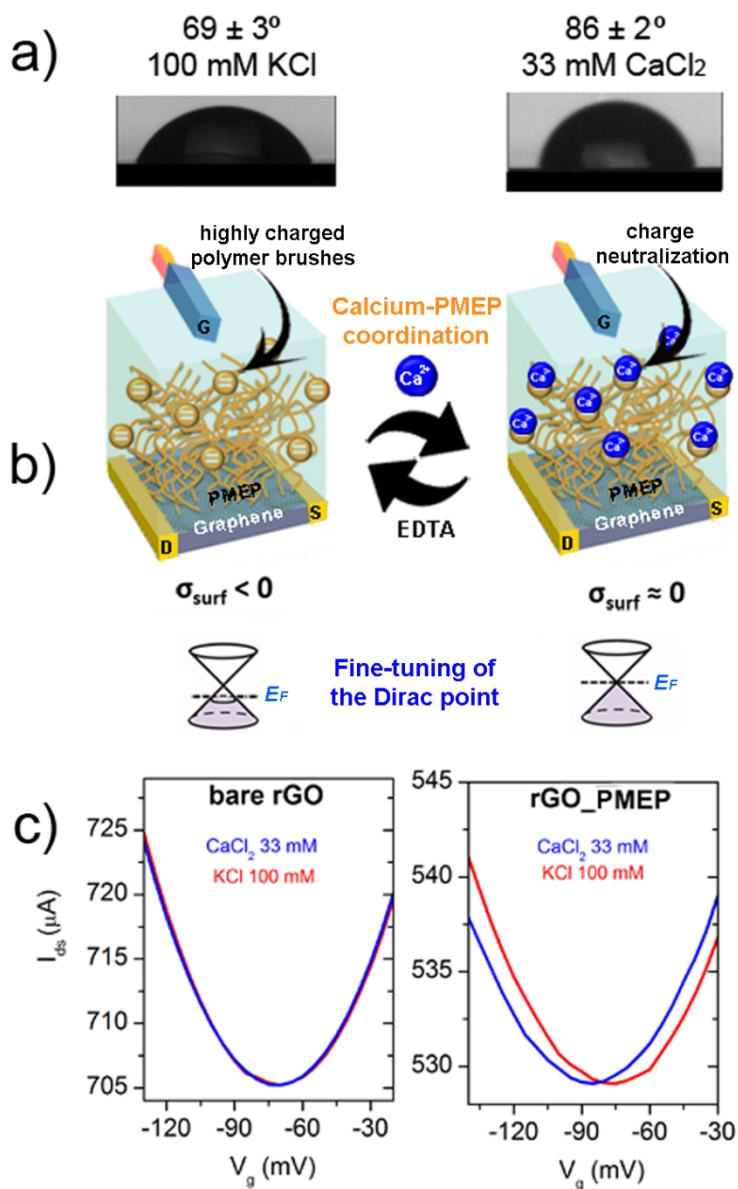




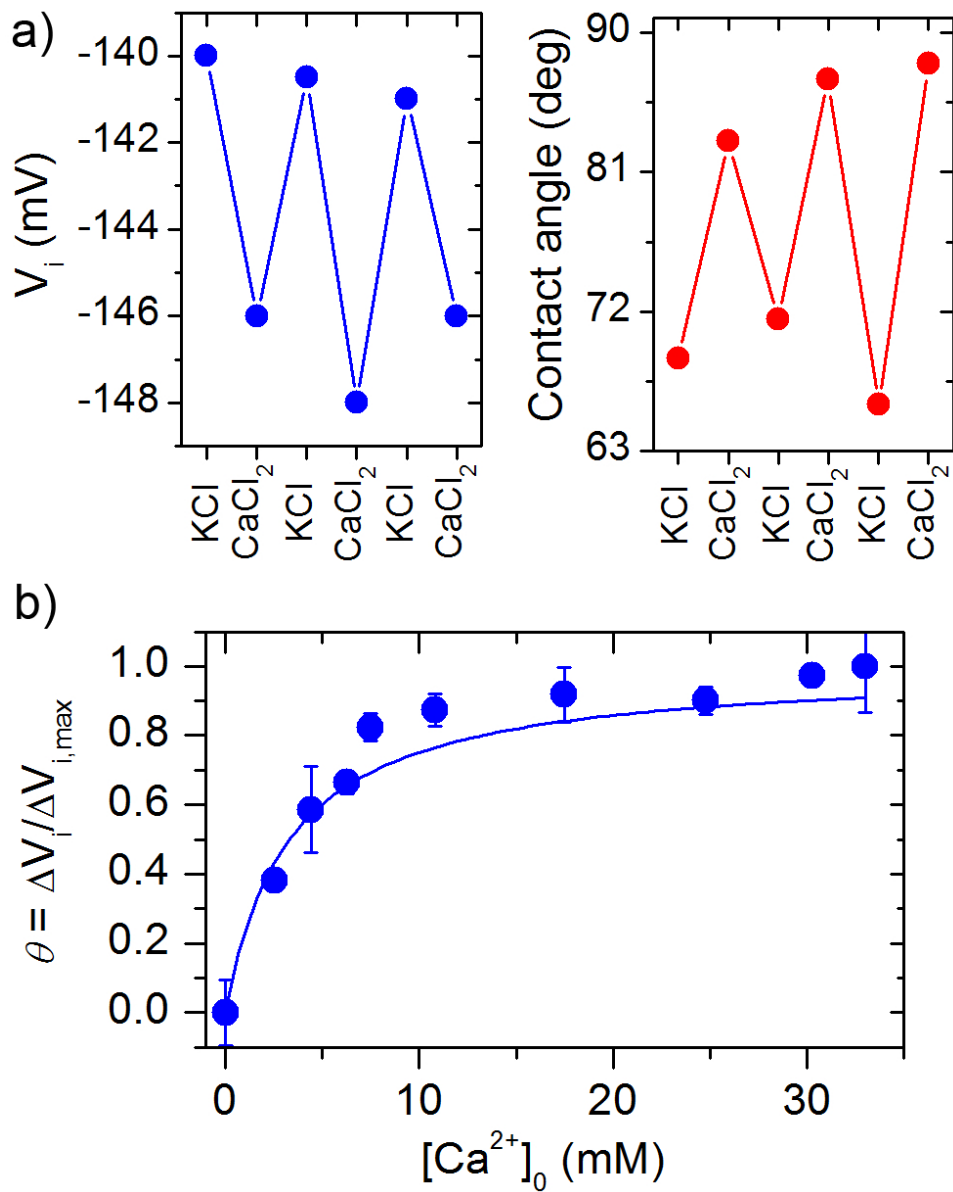
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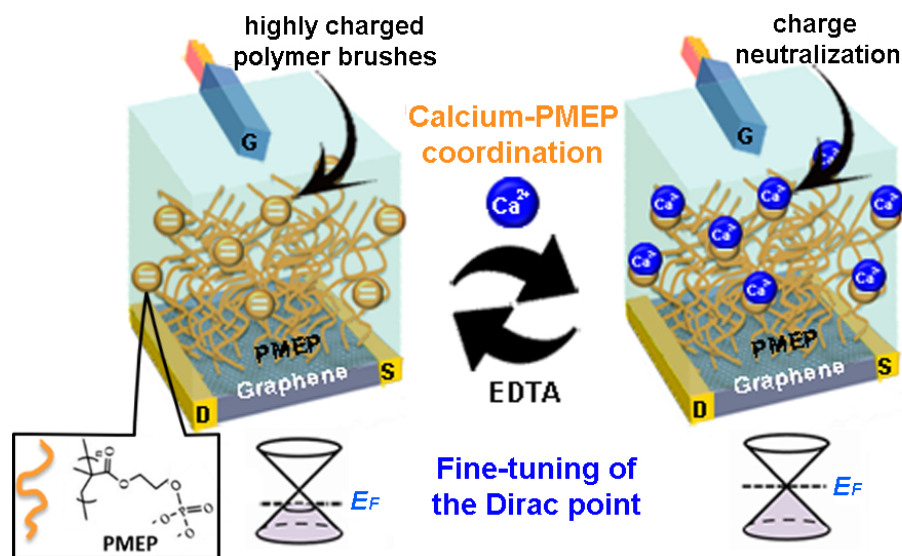
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