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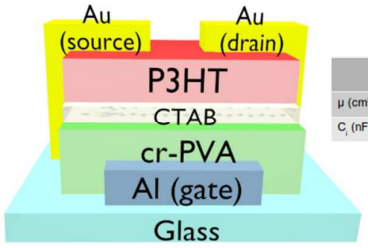
Surfactant treatment of the poly(vinyl alcohol) gate insulator enhances the field-effect mobility of poly(3-hexylthiophene-2,5-diyl) transistors.



	cr-PVA	cr-PVA+CTAB (3.0 mg/mL)
μ ($cm^2V^{-1}s^{-1}$)	0.05	0.48
C_i (nF/cm^2)	23.60	30.92

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Journal Name

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ARTICLE

Poly(3-hexylthiophene-2,5-diyl) Based Field Effect Transistors Performance Enhancement through Surfactant Treatment of the Poly(vinyl alcohol) Gate Insulator Surface

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We report on the improvement of field effect transistors based on Poly(3-hexylthiophene-2,5-diyl) (P3HT) as channel semiconductor and crosslinked poly(vinyl alcohol) (cr-PVA) as gate insulator, through the treatment of the PVA film surface before P3HT deposition. We treated the cr-PVA either with hydrochloric acid (HCl) or with a cationic surfactant, hexadecyltrimethylammonium bromide (CTAB), aiming at the passivation of the hole traps at the cr-PVA/P3HT interface. The treatment with HCl leads to an excessive increase in the transistor leakage current and unstable electrical characteristics, despite implying in an increase of the gate capacitance. The treatment with CTAB leads to transistors with *c.a.* 50% higher specific capacitance and a tenfold increase in the charge carrier field-effect mobility, when compared to devices based on untreated cr-PVA.

Introduction

Organic field effect transistors (OFETs) were intensively investigated over the last years, having their potential low cost and mechanical flexibility as main motivation factors. Following pioneering works [1], substantial effort was devoted to the investigation of different organic semiconductors as channel material and the influence of process conditions on relevant device parameters like field-effect carrier mobility (μ), threshold voltage (V_T), ON/OFF current ratio (I_{on}/I_{off}), among others [2].

Due to the mechanical flexibility, polymeric insulators are especially attractive as gate insulators. Most of the polymers, however, present low dielectric constant and as a consequence, higher driving voltages are required for the operation of OFETs based on such insulators.

Poly(vinyl alcohol), PVA (see Fig. 1), constitutes an interesting alternative for OFETs gate dielectrics, due to the possibility of solution-processing in water, an environmentally friendly solvent. Additional advantages are the relatively high dielectric constant, low-cost and compatibility with flexible substrates. The addition of crosslinking agents allows the preparation of low thickness crosslinked PVA (cr-PVA) films that simultaneously present high capacitance and low leakage current [3-5].

The gate dielectric and the insulator/semiconductor interface are among the key factors in the developing of OFETs, because the properties of this region determine the charge carrier accumulation in the conducting channel. In FETs that use cr-PVA as gate insulator and Poly(3-hexylthiophene-2,5-diyl) (P3HT) (see Fig. 1) as channel semiconductor the presence of charge traps at the P3HT/PVA interface can be electrically detected [6]. These traps, attributed to hydroxyl and ketone groups [6], are deleterious to the device performance. Thus, there is an effective manner to adjust the characteristics of OFETs (for example charge carrier mobility and threshold voltage) through the control of the chemical species in the insulator surface. The passivation of these species has been conducted, for example, through the use of additional layers on top of the gate dielectric or by application of a pre-bias at the gate electrode [7,8].

Quite recently, it was demonstrated that the insertion of a very thin layer of low conductivity aged PEDOT:PSS (poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)) treated with dimethyl sulfoxide, as secondary doping agent, between the cr-PVA and the P3HT channel positively affects the FET performance due to trap action suppression [9]. Despite providing insights to control the traps promoted device characteristics degradation through a very thin shielding layer, aged PEDOT:PSS is not easily available and for this reason cannot be seen as a simple and largely applicable solution.

The physical essence of the problem is that negatively charged sites located in the PVA near to the PVA/P3HT interface are potential trapping sites for the positive charge carriers transiting in the p-type P3HT channel at the interface. The problem is physically complex because the potential energy lowering at the interface on the transport able P3HT molecules, which may lead to self-trapping sites, depends on the position (positional disorder) and neighborhood distribution of negative charges inside the PVA. This leads to a distribution of trap binding energies (energetic disorder). The solution, however, is

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conceptually simple, since it may be in principle only necessary to neutralize the negative charged sites.

The exposition of the surface to HCl vapor is one simple strategy that can contribute to reduce the negative charge at the surface [10]. The HCl decomposition at a surface, however, results in small ions that may potentially diffuse inside the polymeric gate insulator layer, diminishing the insulation capability of the layer.

Bigger molecules would be less susceptible to diffuse through the gate insulator. Hexadecyltrimethylammonium bromide, CTAB (see Fig. 1), is a cationic surfactant consisting of hydrophobic tails and hydrophilic heads. As a consequence, it is an attractive candidate for neutralization of cr-PVA surface negative charges and modification of the P3HT/cr-PVA transport characteristics. Since P3HT is hydrophobic, the hydrophobic tails of CTAB adsorbates tend to stay close to the P3HT surface, while the hydrophilic heads prefer to remain hydrated or linked to negative charges and away from P3HT.

Properties related with aqueous solution of CTAB have been investigated in a number of ways, such as density and light scattering measurements, viscosity [11], conductivity measurements [12] or by adsorption on different substrates [13,14]. When dissolved in water, CTAB shows the tendency to present micelle formation above certain concentration and temperature. A physical-chemical important coordinate in the concentration versus temperature diagram is the Krafft point [15]. The Krafft point is most often understood as the temperature where the solubility versus temperature curve intersects the critical micelle concentration versus temperature curve [16,17]. Owing to the nature of the surfactant having a long alkyl chain, the solubility is limited below the Krafft temperature, whereas, micelles formation occurs above the Krafft temperature [15], which for CTAB equals 25 °C [18].

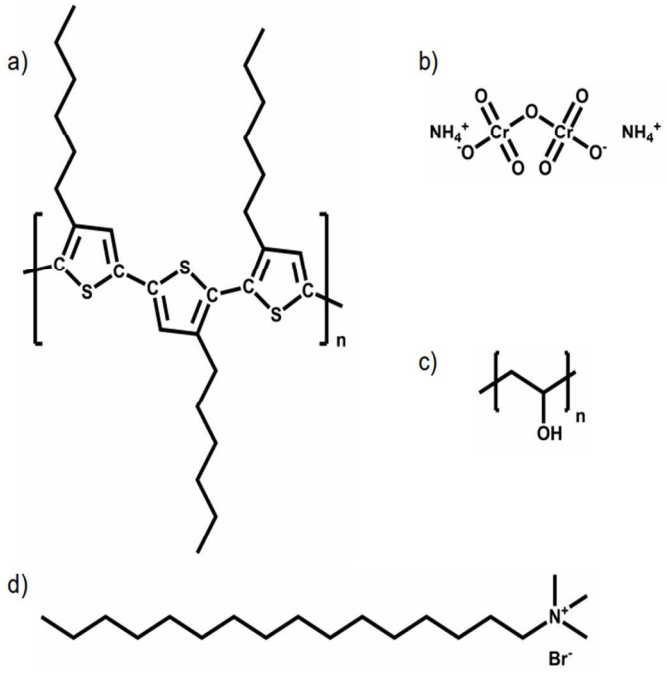

Figure 1. Structures of the chemical compounds used in this work: (a) Poly(3-hexylthiophene-2,5-diyl) (P3HT); (b) Ammonium dichromate (AD) (c) Poly(vinyl alcohol) (PVA) and; (d) Hexadecyltrimethylammonium bromide (CTAB).

In this contribution we report on the preparation of Al-bottom-gate Au-top-source and -drain OFETs with cr-PVA gate insulator and P3HT channel semiconductor (see Fig. 2). We compare devices in which the gate dielectric surface was submitted to HCl vapor treatment or CTAB treatment with those of untreated cr-PVA based devices.

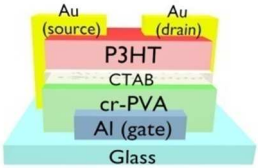

Figure 2. Schematic structure of the OFETs reported in this work.

Results and discussion

The transistors were characterized measuring the output and the transfer current characteristics. Figures 3, 4 and 5 show the results obtained with untreated cr-PVA samples, cr-PVA samples treated with HCl and samples treated with CTAB respectively. The device characteristics of Fig. 3 are shown for comparison, as reference.

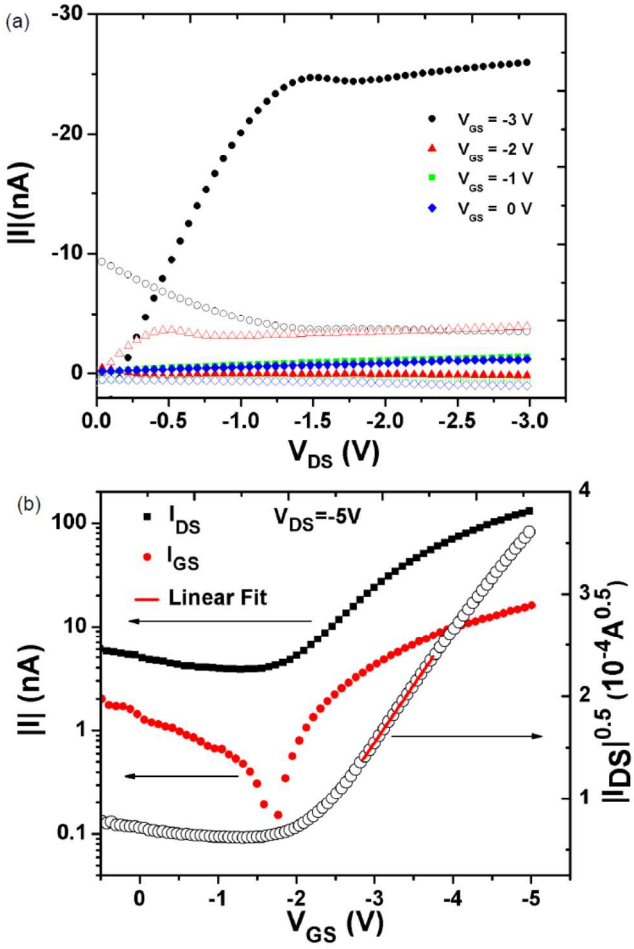

Figure 3. (a) Output characteristics ($I_{DS} \times V_{DS}$) of the transistor untreated cr-PVA layer. Open symbols correspond to ($I_{GS} \times V_{DS}$); (b) transfer characteristics of the same device.

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It can be seen from Fig. 4(a) that the transistors treated with HCl present current modulation, but the curves do not cross each other at the same point, which is an indication of high leakage current (I_{GS}). The output characteristics of the transistor based on cr-PVA treated with HCL (Fig. 4(a)) also show less stable and noisy electrical characteristics. It is evidenced in the transfer characteristics (Fig. 4(b)) that the leakage current (I_{GS}) is higher than the source-drain current (I_{DS}). This condition results in an incorrect μ value determination when the liner fit is applied to the I_{DS} curve segment that corresponds to the linear regime, $I_{DS} = (W/2L)C_i\mu(V_{GS} - V_T)^2$ (W is the channel width, L is the channel length and C_i is the capacitance per unit area) [2], as is the case in Fig. 4 of the present work. This happens because the quasi-linear regime is observed just in the region where $I_{GS} > I_{DS}$, as can be seen in Fig. 4(b). However, it is important to mention that the C_i value shows an increase with respect to untreated cr-PVA, suggesting that the exposure to HCl is promoting at least a partial passivation of the charge traps at the interface.

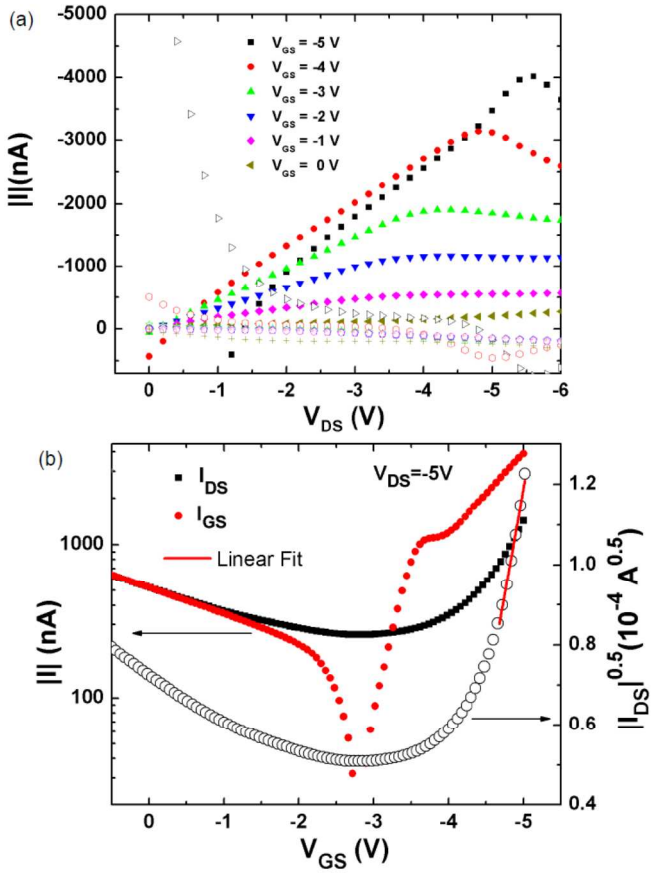

Figure 4. (a) Output characteristics of the transistor in which the cr-PVA layer was treated with HCl. Open symbols correspond to ($I_{GS} \times V_{DS}$); (b) transfer characteristics of the same device.

To avoid the diffusion into the insulator and the consequent poor gate insulation, the cr-PVA surface was alternatively treated with CTAB, since CTAB is a bigger molecule and as a consequence, a negligible diffusivity of CTAB in the cr-PVA is expected. The results obtained from transistors treated with CTAB at a concentration of 3.0 mg/mL are presented in Fig. 5 and in Fig. 6 we present the corresponding AFM image of the cr-PVA/CTAB surface. The AFM image shows that most of the cr-PVA surface is covered by the CTAB when concentration of 0.5 (not shown here) and 3.0 mg/ml are used, forming connected agglomerates, possibly of micelles. The output and transfer characteristics of devices in which the cr-PVA was treated with CTAB concentrations of 0.3 and 0.5 mg/mL were also measured. Note that we considered concentrations below and above the critical micelle concentration of CTAB, which equals 0.36 mg/mL. The results are summarized in Table I. Output and transfer characteristics obtained with samples prepared with 0.3 and 0.5 mg/mL CTAB are shown in the supplementary material.

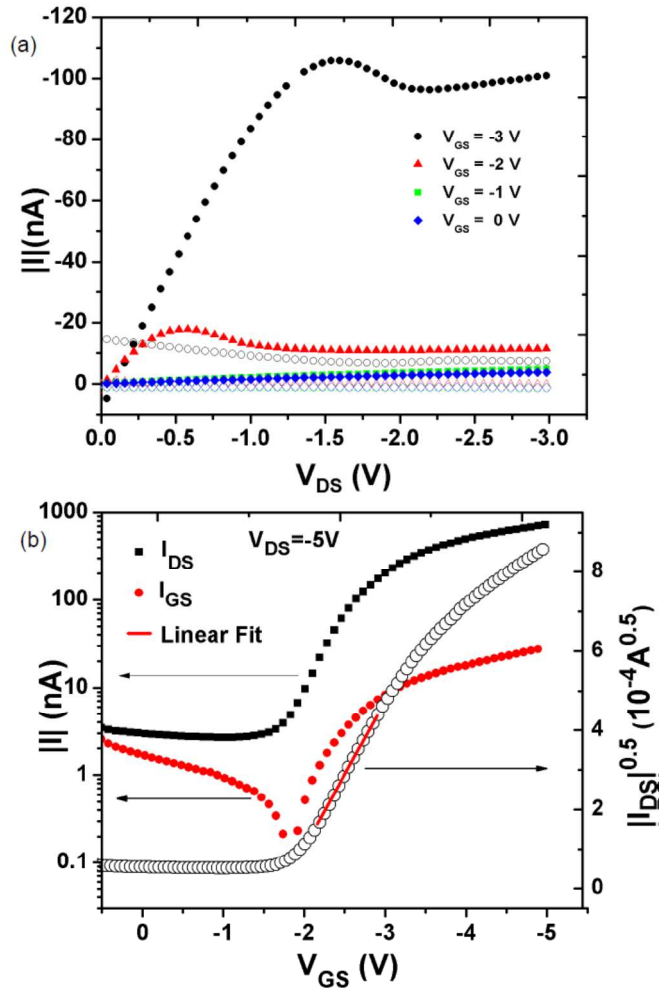

Figure 5. (a) Output characteristics of the transistor in which the cr-PVA layer was treated with 3.0 mg/mL CTAB solution. Open symbols correspond to ($I_{GS} \times V_{DS}$); (b) transfer characteristics of the same device.

Table I. Transistor characteristics calculated for the transistors with untreated cr-PVA, cr-PVA treated with HCl and cr-PVA treated with CTAB at different concentrations.

Sample	V_T (V)	μ (cm^2/V.s)	C_i (nF/cm^2)	I_{on}/I_{off}
untreated cr-PVA	-1.34	0.05	23.60	55
cr-PVA /HCl	-	-	25.57	-
cr-PVA/CTAB (0.3 mg/mL)	-1.60	0.04	23.24	94
cr-PVA /CTAB (0.5 mg/mL)	-1.73	0.09	30.31	190
cr-PVA /CTAB (3.0 mg/mL)	-1.82	0.48	30.92	310

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To be absolutely sure that the leakage current did not influence the extracted parameters leading to an incorrect value, we repeated the calculation of the parameters of Table I for the two more extreme possible cases: we calculate the parameters using the curves (I_{DS} + I_{GS}) and (I_{DS} - I_{GS}) instead of I_{DS}, obtaining the same values as in Table I.

The broad peaks observed in the output characteristics of our devices are usually attributed to water and oxygen presence [19]. This is in principle expected, since we did not measure our devices in vacuum. Devices were characterized in laboratory ambient atmosphere.

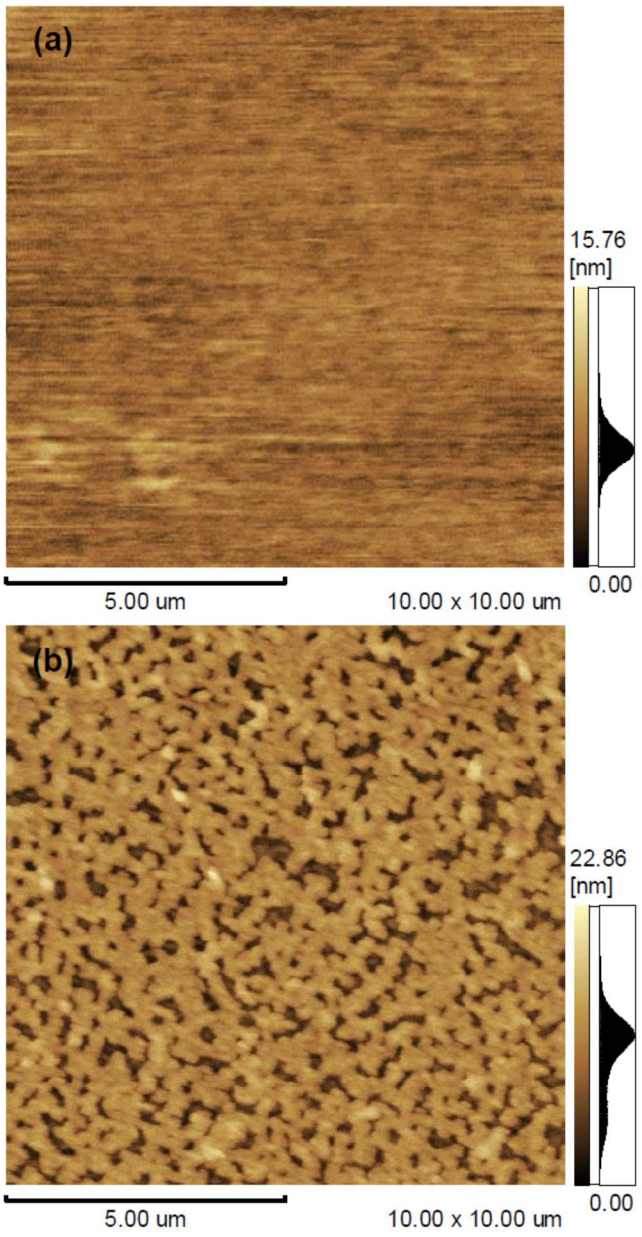

Figure 6. AFM image of a cr-PVA layer treated with (a) 0.3 mg/ml and; (b) 3.0 mg/mL CTAB solution.

Our results demonstrate that the treatment of the cr-PVA with a surfactant solution constitutes an effective procedure for the transistor performance enhancement. It must be mentioned that until the moment we only investigated the use of one type of surfactant. The nature of the hydrophilic head is important since it may determine the effectiveness of the trap neutralization and interface passivation. The size of the hydrophobic tail may also have consequences on the morphology of the treated cr-PVA surface and as a consequence, on the morphology of the P3HT deposited onto the cr-PVA, also modifying the interface and the charge transport near to the interface. The presence of CTAB enhances the wetting properties of the cr-PVA surface. The contact angle decreases from 57.1° in cr-PVA to 41.8° in case of 3.0 mg/mL CTAB treatment of the cr-PVA surface, suggesting water capture from the cr-PVA surface by the surfactant. In this context, much more work is necessary to deeply understand the molecular arrangement at the interface and its consequences on trap passivation and mobility enhancement.

The deposition of the CTAB solution was made using a solution at 60 °C, which is above the Kraft temperature (25 °C). Under this condition, micelles are formed in the solution when the concentration is above the critical micelle concentration (0.36 mg/mL). In this sense it is interesting to note that the increment in C_i occurs for CTAB treatment using solutions with (CTAB concentration of 0.5 and 3.0 mg/mL), indicating that a low CTAB concentration is enough for the interface trap passivation. However, the mobility is increased by a factor ~2 by the use of CTAB, showing only a slight increase when the critical micelle concentration border is crossed. But a pronounced enhancement is observed for the case of 3.0 mg/mL CTAB treatment (despite C_i values similar to other CTAB concentration treatments), which is a clear indication that another mechanism is also contributing for this increase. We tentatively attribute this mobility increase to modifications in the interface morphology due to the presence of the hydrophilic tails of the CTAB, which seem to positively affect the molecular conformation and arrangement of the P3HT molecules, possibly reducing conformation dependent self-trapping in the P3HT molecules.

Experimental

Transistors were prepared using bottom-gate top-contact geometry on soda lime glass substrates. The substrates were sequentially washed in acetone, ultrapure deionized water (resistivity >18.2 MΩ/cm) and isopropanol in an ultrasonic bath. The gate electrode was obtained by evaporating a 100 nm thick Al layer, patterned with a shadow mask, on top of the glass substrate at base pressure of 4 × 10^{-6}Torr. The gate insulator was prepared using PVA, as received from Sigma-Aldrich (MW = 130,000 amu). PVA was dissolved in ultra-pure deionized water at a concentration of 60 mg/mL and stirred for one hour at 60°C. Ammonium dichromate (AD) was then added to the PVA solution at a PVA:AD weight ratio of 1:0.25.The PVA-AD layer was spin coated on top of the patterned Al/glass at 4000 rpm for 60 s to obtain a 300 nm thick layer. The crosslinked PVA-AD layer (cr-PVA) was obtained by exposing the film to ultra-violet light (wavelength of 365 nm, 8 W) for over 10 min, after which it was thermally annealed for 1 hour at 100°C in vacuum. After the gate insulator preparation, some samples were submitted to a treatment with HCl or CTAB.

The regioregular P3HT, rr-P3HT (Sigma-Aldrich, regioregularity > 90%) was used as received. The solution was prepared in toluene at a concentration of 8 mg/mL using magnetic stirring at 60°C. The P3HT layer was spin-coated onto the cr-PVA/CTAB or HCl treated cr-PVA layer at 1500

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rpm, for 60 s, to obtain a 40 nm thick layer. It was then thermally annealed at 100°C in vacuum for 30 min.
Finally, a 100 nm thick gold layer patterned using a shadow mask was evaporated onto the P3HT films at a base pressure of 4×10^{-6} Torr, as top electrodes. Devices were prepared with L = 100 μm and W = 2 mm. Thickness measurements were done using the Bruker DektakXT surface profiler. Finally, the surface morphology of the samples was characterized using a Shimadzu SPM-9500J3 atomic force microscope (AFM). Contact angle measurements were performed using an OCA 15 plus Filderstadt tensiometer.
Capacitance was measured in a Al/cr-PVA/Al sandwich structure for treated and untreated cr-PVA using an Agilent 4284 A LCR meter operating at a frequency of 1 kHz and the transistors were electrically characterized using a programmable Keithley 2602 dual source meter, under dark room conditions in laboratory ambient atmosphere.
Gate insulator treatment with HCl The samples were exposed to HCl vapor facing the cr-PVA to the liquid HCl in a becker at room temperature for 30 s and in the sequence the samples were dried in a hotplate during 5 min at 60 °C.
Gate insulator treatment with CTAB CTAB was dissolved in ultra-pure deionized water at a concentration of 0.3, 0.5 and 3 mg/mL. The CTAB solution was magnetically stirred for 1 hour at 60°C and sequentially spin-coated onto the cr-PVA layer at 1500 rpm, for 60 s, to obtain an approximately 6, 15 and 15 nm thick layer for the 0.3, 0.5 and 3 mg/mL concentration films, respectively (see Fig. 6). The films were again thermally annealed at 100°C for 30 min in vacuum.

Conclusions

We demonstrated that the performance of organic field effect transistors can be enhanced through chemical treatment of the gate insulator surface. The use of HCl or CTAB treatment on cr-PVA gate insulator leads to an increase in the capacitance of the devices. This increase, which is more pronounced in the case of CTAB, is due to the passivation of charge traps located at the cr-PVA interface. The use of surfactant also leads to an increase of the field effect charge carrier mobility that we attributed to the hydrophilic tail of CTAB, which is more pronounced in case of devices submitted to the treatment with the higher used CTAB concentration.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Output and transfer characteristics of the transistors prepared with untreated cr-PVA and cr-PVA treated with CTAB at concentration of 0.3, 0.5 and 3.0 mg/mL). See DOI: 10.1039/b000000x/

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