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ARTICLE

Low Voltage Electrolyte-Gated Organic Transistors Making Use of High Surface Area Activated Carbon Gate Electrodes†

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In electrolyte-gated transistors, the exceptionally high capacitance of the electrical double layer forming at the electrolyte/transistor channel interface permits current modulations of several orders of magnitude, at relatively low gate voltages. The effect of the nature of the gate electrode on the performance of electrolyte-gated transistors is still largely unclear, despite recent intensive efforts. Here we demonstrate that the use of high surface area, low cost, activated carbon gate electrode enables low voltage (sub-1 V) operation in ionic liquid-gated organic transistors and renders unnecessary the presence of an external reference electrode to monitor the channel potential, thus dramatically simplifying the device structure. We used the organic electronic polymer MEH-PPV (poly[2-methoxy-5-(2'-ethylhexyloxy)-p-phenylene vinylene), as the channel material, and the high ionic conductivity, low viscosity ionic liquid [EMIM][TFSI] (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide), as the electrolyte gating material. We believe that this will prove to be the first of a new generation of low voltage electrolyte-gated transistors for applications in organic printable electronics.

Introduction

Electrolyte-gated (EG) transistors[1–3] make use of electrolytes, such as polymer electrolytes, ionic liquids and ion gels,[4] to replace conventional dielectrics in large area, flexible electronic applications.[5,6] EG transistors exhibit current modulations of several orders of magnitude at relatively modest gate voltages, exploiting the exceptionally high capacitance of the electrical double layer formed at the electrolyte/transistor channel interface. Different doping mechanisms, including electrostatic and Faradaic (the latter being commonly referred in the electrolyte gating literature as electrochemical doping), have been proposed to explain the gating process in EG transistors. While both processes can be reversible, the former does not involve charge transfer and takes place in the immediate vicinity of the surface of the channel material, whereas the latter involves charge transfer and takes place in the bulk of the channel material.

A number of channel materials have been used in EG transistors, including organic single crystals,[7–9] organic thin films of small molecules and polymers,[10–14] thin films of metal oxides,[15–20] InN,[21] CdSe,[22] and PbSe.[23] The nature of the channel material is one of the key factors establishing the type of doping mechanism. For channel materials based on organic polymers, it is mainly Faradaic. For this class of channel materials, the doping charge and the (pseudo)capacitance are about two orders of magnitude larger than for electrostatically doped, non-porous materials.[24] Importantly, because of the Faradaic nature of the doping, in polymer channels the level of the doping and, hence, the current modulation depend upon the channel electrical potential. As a consequence, to optimize the current modulation in EG transistors based on organic polymer channels, it is of the utmost importance to carefully monitor and set the channel potential vs an additional reference electrode. Further, it is necessary to monitor the voltage in order to ensure its compatibility with the electrochemical stability window of the electrolyte.

The effect of the nature of the gate electrode on the performance of EG transistors is still largely unclear, at present, despite recent intensive efforts.[13,25] However, a judicious choice of the gate electrode material can limit undesirable electrochemical reactions at the gate electrode, detrimental for the device stability. In addition, gate electrodes with high specific surface area are desirable for high current modulations in transistor channels prone to bulk electrochemical doping, such as organic polymers. Indeed, high surface area gate electrodes featuring high double layer specific capacitances should be non-limiting in terms of their capability to supply within a narrow potential excursion the charge required to dope organic polymer transistor channels.

High surface area, low cost electrodes made of activated carbon (1000 - 2000 $m^2 \cdot g^{-1}$) have been successfully employed in double-layer supercapacitors.[24,26] They store charge by a fast, highly reversible electrostatic process described by $Q = C\Delta Vm$, where Q is the stored charge, C is the specific capacitance (ca 100 - 200 $F \cdot g^{-1}$ for optimized high surface area carbon), ΔV is the electrode potential excursion, and m is the mass of the electrode material. Gate electrodes based on activated carbon with high mass and specific capacitance are attractive candidates for application in EG transistors. Indeed, within a relatively low ΔV (a few mV), they can store electrostatically an amount of charge that, counterbalanced at the transistor channel, leads to its effective doping. At the same time, the low value of ΔV employed opens the possibility to use the carbon gate electrode as a quasi reference electrode.[27] The use of high surface area activated carbon gate electrodes represents an exciting approach to achieve low voltage channel modulations. A *caveat*, of course, has to be considered for this approach. The redox activity of the channel material has to take place at low potentials vs the carbon

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quasi reference electrode (i.e. to demonstrate EG transistors with sub-1 V operation voltage, the redox activity of the polymer has to take place at potentials lower than 1 V vs the carbon quasi reference electrode).

In this work we demonstrate that the use of a high surface area, low cost, activated carbon gate electrode makes low voltage (sub-1 V) operation in ionic liquid-gated organic transistors possible and renders unnecessary the presence of an external reference electrode to monitor the channel potential. We use the organic electronic polymer MEH-PPV, poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene],[11,13] channel material. The electrolyte gating material is the high ionic conductivity, low viscosity ionic liquid [EMIM][TFSI] (1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide). We believe that this will prove to be the first of a new generation of low voltage EG transistors for applications in organic printable electronics.

Results and discussion

The structure of the EG transistors investigated in this work is shown in Fig. 1. The MEH-PPV thin film, deposited on the source-drain pre-patterned SiO_2 substrate (source-drain distance, L, 10 μm and electrode width, W, 4 mm) is vertically stacked with the activated carbon gate and separated from it by a Durapore® filter soaked in the ionic liquid electrolyte.[28] An additional activated carbon electrode, the quasi reference electrode,[27] is placed to the side of the activated carbon gate electrode. The activated carbon gate electrode, with a high specific capacitance of about 100 F·g^{-1} in [EMIM][TFSI],[26,29] supplies the charge required to dope the MEH-PPV channel by a fast, highly reversible electrostatic process.

We used about 1 mg of activated carbon per cm^2 of geometric area of the gate electrode in order to keep its potential within a few tenths of mV vs that of the reference electrode, during channel modulation. This, in turn, creates the possibility of using the activated carbon gate electrode itself as a quasi reference electrode for channel potential modulation, therefore rendering the use of the external quasi reference electrode unnecessary during transistor measurements. To verify that the carbon gate electrode can behave as a quasi reference electrode we performed a cyclic voltammetry survey. Fig. 2a shows cyclic voltammetry plots obtained using the MEH-PPV thin film as the working electrode and the activated carbon gate as the counter electrode (CE). The black curve was obtained using a supplementary, relatively small, activated carbon quasi-reference electrode (RE) whereas the dashed red curve was collected considering the gate electrode as both the CE and the quasi RE. In the latter case, the working electrode potential corresponds to -V_{gs} (V_{gs} being the gate-source voltage). The voltammetric cycles performed in the two cases (with lateral quasi reference or without i.e. with the gate acting as the quasi reference) almost overlap.[30] More important, Fig. 2a shows that the MEH-PPV doping process takes place between about 0.3 V and 1 V vs the activated carbon quasi reference electrode, suggesting that a gate-source voltage bias lower than 1 V is necessary for the operation of the EG transistor.
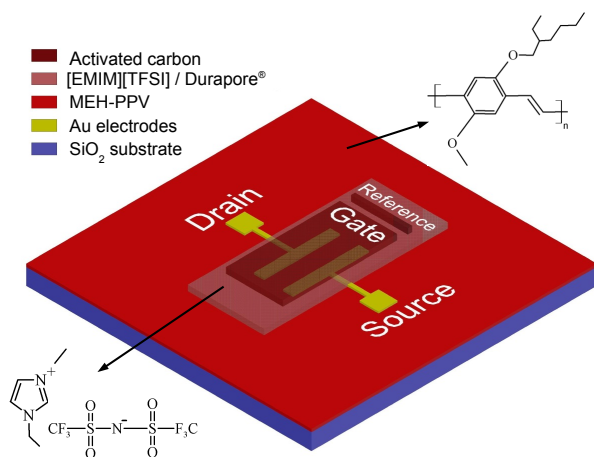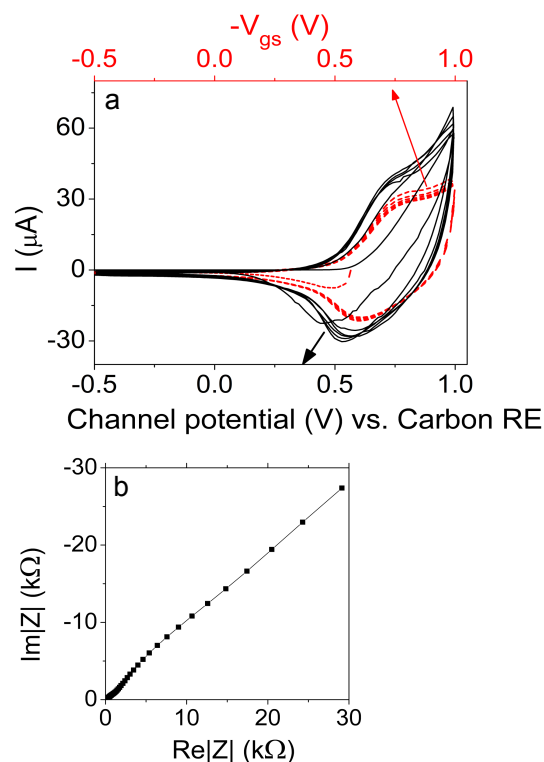

Fig. 1 Device structure of the [EMIM][TFSI]-gated MEH-PPV transistors making use of an activated carbon gate electrode, in this work. The structure includes an activated carbon quasi reference electrode. A separator (Durapore® membrane filter, 9 mm × 4 mm × 125 μm) was soaked with [EMIM][TFSI] and placed on top of the MEH-PPV transistor channel (source-drain interelectrode distance, L, 10 μm, and electrode width, W, 4 mm). Two conducting carbon papers coated with activated carbon were set in contact with the separator and used as the gate (6 mm × 3 mm × 170 μm) and quasi reference (6 mm × 1 mm × 170 μm) electrodes. The molecular structures of the polymer MEH-PPV and the [EMIM][TFSI] ionic liquid are shown.

Fig. 2 Electrochemical characteristics of [EMIM][TFSI]-gated MEH-PPV transistors. (a) Cyclic voltammetry at 50 mV·s^{-1} obtained using the polymer film as the working electrode, the activated carbon gate electrode as the counter electrode and a second activated carbon electrode as the quasi reference electrode (black, solid line) or the carbon gate electrode itself as both the counter and the quasi reference electrode (red dotted line). In the latter case, the potential of the transistor channel corresponds to -V_{gs} (V_{gs} being the gate-source voltage). (b) Nyquist plot of the MEH-PPV working electrode at 0.8 V vs activated carbon, with the activated carbon gate electrode as the counter electrode and the small-sized activated carbon electrode as the quasi reference electrode.

The cyclic voltammetry plots obtained using the quasi reference electrode (solid curves in Fig. 2a) show that the absolute value of the current increases for the first two voltammetric cycles, after which, from the third to sixth cycle, they almost overlap. The increase in the current from the first to the second cycle is attributable to an increased possibility for ions of penetrating the polymer after swelling caused by doping (forward cycle) and dedoping (backward cycle) of the polymer. From the slope of the linear plot of the doping charge (obtained by the integral of the current during the third cycle over time) vs channel potential, we obtained a pseudocapacitance of 0.83 mF. Electrochemical impedance spectroscopy is a relevant technique to study the mechanism and the limiting steps of the doping process of the polymer channel. Fig. 2b shows the Nyquist plot of the MEH-PPV transistor channel, obtained at 0.8 V vs the activated carbon quasi reference electrode. The impedance of the channel is a 45 ° transmission line typical of diffusion controlled processes related to the diffusion of the doping ions from the viscous ionic liquid into the polymer channel. This suggests that the time response of the transistor is affected by ion diffusion. The pseudocapacitance obtained at 10 mHz is 0.6 mF, slightly lower than the limit capacitance deduced by cyclic voltammetry. The Bode plot (Electronic Supplementary Information, Fig. S1) indicates that the pseudocapacitive behaviour of the polymer becomes predominant in the channel impedance at frequencies lower than 10 Hz, thus indicating a time response of the device > 100 ms.

The electrochemical experiments suggested the possibility of operating our polymer transistors at unprecedented low voltages and the device characterization experiments indeed confirmed the interest of using activated carbon gate electrodes. The output curves (I_{ds}, drain-source current, vs V_{ds}, drain-source voltage, for increasing values of $|V_{gs}|$, Fig. 3a) show that, for our p-type MEH-PPV transistors, the saturation regime is achieved at V_{ds} values as low as –0.2 V. The transfer characteristics of the device in the saturation regime (Fig. 3b) show that the behavior of the gate-source, I_{gs}, current is in agreement with the cyclic voltammetry measurements. The conduction onset is located at about -0.72 V in the forward sweep and -0.44 V in the backward sweep. The hysteresis observed in the transfer curve is attributable to the slow diffusion of the doping ions in the polymer channel, already discussed for the Nyquist plot (Fig. 2b). Indeed, the hysteresis decreased with decreasing the sweep rate, such that, at 10 mV·s^{-1}, the conduction onset is located at -0.66 V in the forward sweep and -0.56 V in the backward sweep (inset Fig. 3b). The transistor current ON/OFF ratio (calculated from I_{ds} at V_{gs} = 1 V (ON) and 0 V (OFF)) was approximately 5×10^3 (Electronic Supplementary Information, Fig. S2).

For our [EMIM][TFSI]-gated MEH-PPV transistors, the hole carrier mobility (μ) was obtained from:

$$\mu = \frac{L}{W} \frac{I_{ds}}{V_{ds}ep} \qquad (1)$$

where e is the elementary charge and p is the charge carrier density (cm^{-2}), deduced from:

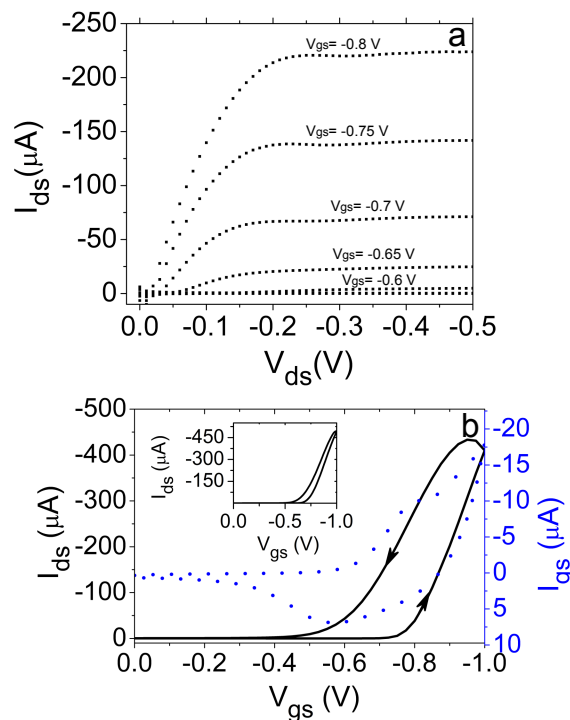$$p = \frac{Q}{eA} = \frac{\int I_{gs}dV_{gs}}{r_v eA} \qquad (2)$$

Fig. 3 Device characteristics of [EMIM][TFSI]-gated MEH-PPV transistors making use of activated carbon for the gate and the quasi reference electrode: (a) output characteristics (I_{ds} vs V_{ds} for V_{gs} = 0, -0.6, -0.65, -0.7, -0.75 and -0.8 V); (b) transfer characteristics in the saturation regime (V_{ds} = -0.3 V), I_{ds} (left axis, solid line) and I_{gs} (gate-source current, right axis, dotted line) plotted vs V_{gs}, sweep rate 50 mV·s^{-1}. Inset: transfer characteristics in the saturation regime (V_{ds}=-0.3 V), for a sweep rate of 10 mV·s^{-1}.

where I_{gs} is the gate-source current (measured during the linear transfer curve, V_{ds} = -0.1 V, Electronic Supplementary Information, Fig. S3), r_v is the sweep rate, and A is the active channel surface area (18 mm^2, surface area of the polymer in contact with the electrolyte, in turn in contact with the gate electrode).[11,31,32] The hole mobility we obtained was (1.0 ± 0.5) ×10^{-2} cm^2·V^{-1}·s^{-1}, in agreement with the literature.[33]

Experimental

Substrates were cleaned by sequential ultrasonic baths in isopropyl alcohol (IPA, J.T. Baker, microelectronic grade, 5 min), acetone (J.T. Baker, microelectronic grade, 10 min), and IPA (5 min), followed by a 5 min dehydration process at 120 °C in N$_2$ atmosphere consisting of 3 purging cycles of low pressure (20 Torr) and high pressure (500 Torr). Drain and source contacts of Ti/Au, 5/40 nm/nm, were photolithographically patterned on SiO$_2$ substrates (channel width, W, 4000 μm and length, L, 10 μm). 5 mg of MEH-PPV (Sigma Aldrich, 55 kDa) in 1 mL of toluene (Sigma Aldrich) were mixed and stirred overnight in a N$_2$ glove box (O$_2$, H$_2$O ≤ 5 ppm) keeping the temperature at about 40 °C. MEH-PPV thin films were deposited by spin coating the solution at 1000 rpm. Afterwards, films were thermally treated at 70 °C for 3 hours. [EMIM][TFSI] (IoLiTec, >99%, ionic conductivity 6.63 mS·cm^{-1} and viscosity 39.4 mPa·s at 20 °C)[34] was purified under vacuum (~10^{-5} Torr) at 80 °C overnight prior to use, and stored (for a maximum period of 2 days) in the N$_2$ glove box. The device fabrication was completed by sandwiching a Durapore® GVHP filter separator soaked in the ionic

liquid between the MEH-PPV thin film and the activated carbon gate electrode. An activated carbon quasi reference electrode was placed on the side of the carbon gate electrode (see Fig. 1). The gate and quasi reference electrodes were prepared using carbon paper (Spectracorp 2050) coated with an ink of activated carbon (PICACTIF SUPERCAP BP10, Pica, 28 mg·mL^{-1}) and polyvinylidene fluoride (PVDF, KYNAR HSV900, 1.4 mg·mL^{-1}) binder in N-methyl pyrrolidone (NMP, Fluka, > 99.0%) solvent. The coating was followed by thermal treatment at 60 °C for several hours to remove the solvent.

The characterization of the EG transistors was carried out in a N_2 glovebox (H_2O, $O_2 \leq 5$ ppm). The electrochemical tests were performed using a PARSTAT 2273 (Princeton Applied Research) multichannel potentiostat equipped with impedance modules. Electrochemical impedance spectroscopy (EIS) was performed at frequencies from 20 kHz to 10 mHz and an oscillation amplitude of 10 mV. Transistor device characteristics were measured using a B1500A Agilent semiconductor parameter analyzer.

Conclusions

In conclusion, we have demonstrated sub-1 V electrolyte-gated transistors making use of high surface area activated carbon as the gate electrode material, [EMIM][TFSI] as the electrolyte gating medium, and MEH-PPV as the organic polymer channel material. The use of the high surface area carbon gate electrode in contact with the ionic liquid renders unnecessary the use of a reference electrode in the device structure. Indeed, the gate electrode itself can be employed as quasi reference electrode. The processability of both the carbon gate electrode and polymer channel is of relevance for the development of flexible miniaturised devices. For the simple architecture and the low operation voltages, we believe that the devices we report have the potential to advance the development of low cost, large area electronics.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Bode plot of MEH-PPV working electrode at 0.8 V vs activated carbon (Fig. S1), logarithmic plot of the transfer curve in the saturation regime (Fig. S2) and transfer curve in the linear regime (Fig. S3). See DOI: 10.1039/b000000x/

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