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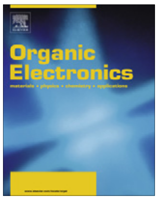

Water-gated organic nanowire transistors

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The remaining authors report with great sadness the passing of our co-author Tim Richardson shortly before publication. We wish to dedicate this work to the memory of a much missed colleague and friend.

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ABSTRACT

We gated both p-type, and n-type, organic nanowire (NW) films with an aqueous electric double layer (EDL) in thin-film transistor (TFT) architectures. For p-type NWs, we used poly(3-hexylthiophene) (P3HT) NWs grown via two different routes. Both can be gated with water, resulting in TFTs with threshold lower than for conventionally cast P3HT films under the same gating conditions. However, TFT drain currents are lower for NWs than for conventional P3HT films, which agrees with similar observations for 'dry' gated TFTs. For n-type NWs, we have grown 'nanobelts' of poly(benzimidazobenzophenanthroline) (BBL) by a solvent/non-solvent mixing route with later displacement of the solvent, and dispersion in a non-solvent. Water-gating such films initially failed to give an observable drain current. However, BBL nanobelts can be gated with the aprotic solvent acetonitrile, giving high n-type drain currents, which are further increased by adding salt. Remarkably, after first gating BBL NW films with acetonitrile, they can then be gated by water, giving very high drain currents. This behaviour is transient on a timescale of minutes. We believe this observation is caused by a thin protective acetonitrile film remaining on the nanobelt surface.

1. Introduction

A thin-film transistor (TFT) architecture has been widely used in particular with non-conventional semiconductors, e.g. amorphous Si [1], organic semiconductors (OSCs) [2], and precursor-route inorganic semiconductors [3,4]. Therein, a thin film of an intrinsic (i.e., undoped) semiconductor is gated by a voltage applied to a gate electrode that is not directly in contact with the semiconductor, but separated from it via a gate medium. When the gate voltage exceeds a threshold, the 'field effect' generates a charge carrier accumulation layer at the semiconductor/gate medium interface, with a resulting increase in conductivity up to several orders of magnitude. The properties of the gate medium, in particular its specific capacitance and density of carrier traps at the insulator/semiconductor interface, are crucially important to the TFT's performance [2,5]. Traditionally, the gate medium was a solid dielectric. Recently, however, electrolytes have also been used as gate media. Under applied gate voltage, mobile ions form an electric double layer (EDL) at the gate medium/semiconductor interface, which displays very high specific capacitance, generating a strong electric field near the interface, even at gate voltages below 1 V. Solid electrolytes and ionic liquids have been used as gate media for hole [6,7] – as well as electron-transporting [8] OSCs. An interesting development is the discovery of Kergoat et al. that even deionised (DI) water can act as a gate medium for OSCs [9]. This discovery has inspired attempts to develop OSC-based TFT sensors for the detection of waterborne analytes, wherein the water sample under investigation is used as the TFT's gate medium [10]. The specific capacitance of the EDL in deionised water has been estimated as 3 μF/cm^2 [9]; however, the capacitance of EDLs is a notoriously complicated function of frequency, geometry and ion

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concentration [11], and this figure is best taken only as an order-of-magnitude estimate.

Another recent line of OSC TFT research is the introduction of organic nanowires (NWs). NWs are long, needle-shaped crystals that may grow when some OSCs (namely those with a slip-stacked crystal motif) undergo suitable physicochemical treatment while in solution, e.g. thermal cycles, or addition of non-solvent. Depending on the material, and growth conditions, some variations on the NW morphology have also been observed, e.g. flat ‘nanobelts’ [12] or curved ‘nanofibres’ [13]. We will here refer to all of these related morphologies as ‘nanowires’ as generic term, except when discussing a specific sample. After formation, NWs may form stable suspensions in their growth medium and can be processed into films by spin- or drop-casting, similar to film deposition from OSC solutions. However, the morphologies of resulting films are distinctly different from the smooth, uniform films obtained when casting OSCs from proper solutions. Depending on casting conditions and NW density in the growth medium, films may contain isolated single wires, lightly overlapping wires or a dense multilayer NW ‘mesh’. The literature on organic NWs (and related morphologies) includes many reports on TFTs; these have been comprehensively reviewed by Briseno et al. [14].

The NW morphology implies a large OSC surface area, and consequently, has led to remarkable sensitivity enhancement of chemiresistor devices that employ NWs, compared to devices using the same OSC in the form of uniform, solution-cast films [13,15]. It is therefore tempting to implement organic NWs as the active layer in electrolyte-gated OSC TFTs. To date, however, no electrolyte-gated NW OSC field-effect TFTs have been reported. The work of Wanekaya et al. [16], despite its title, does report on an organic electrochemical transistor (OECT), rather than a field effect transistor, and requires a strongly acidic medium. For the classification, and relative merits, of OECTs vs. organic TFTs, see for example the reviews of Inganäs [17], and Owens and Malliaras [18].

Here, we demonstrate water-gated organic NW field-effect TFTs using NWs grown from both p-type, and n-type, OSCs. As p-type organic semiconductor, we have chosen regioregular poly(3-hexylthiophene) (P3HT), an OSC widely used for organic TFTs [2]. P3HT is also known for its ability to grow NWs [19], and water-gated field effect TFTs using P3HT films cast from chloroform have been demonstrated by Kergoat et al. [9]. As n-type organic semiconductor, we have selected poly(benzimidazobenzophenanthroline) (BBL). BBL can act as n-type material in organic TFTs with good mobility ($\mu_e = 0.1\ \mathrm{cm^2/Vs}$) [20], and Briseno et al. [12] have reported on the growth of BBL ‘nanobelts’. BBL possesses a rather deep ‘lowest unoccupied molecular orbital’ (LUMO) of −4.0 eV [21], which allows reasonable electron injection even from high work function metals, and may make BBL consistent with water-gating, despite the potential trapping of electrons by water and/or oxygen: Nicolai et al. [22] recently suggested from theoretical calculations that such trapping can be avoided when the LUMO is more than 3.6 eV below vacuum level.

2. Experimental

2.1. Nanowire growth

“CB-P3HT” NWs were grown from regioregular P3HT (rrP3HT) (sourced from Ossila) in 5 mg/ml chlorobenzene (CB) solution. CB was initially heated to 80 °C and agitated to allow solution; solutions were then filtered through a 0.45 μm PTFE syringe mounted filter, and left to mature in the dark at ambient temperature for several weeks or months. “Anisole-P3HT” NWs were prepared via a variation on the whisker method [19]. 5 mg of rrP3HT (sourced from ADS dyes) were dissolved in 1 ml of Anisole. The solution was heated to 90 °C until fully dissolved and allowed to cool to room temperature over a duration of approximately 1 h, and then left to mature for 3 days. Thermal cycles and maturing were carried out in sealed bottles to avoid solvent evaporation. “BBL” nanobelts were grown from poly(benzimidazobenzophenanthroline) (BBL) (sourced from Sigma Aldrich) dissolved at 0.2 mg/ml in methane sulphonic acid (MSA). BBL nanobelt growth was driven by the drop-wise addition of a non-solvent mixture (chloroform/methanol 4:1) to the solution of BBL in MSA whilst stirring continuously, as described in [12]. Due to the strong (acid/base) interactions between MSA and BBL, it is likely that some residual MSA remains incorporated in the resulting BBL NWs; however, this will also be the case for BBL films cast from MSA (cf. the casting procedure reported by Babel and Jenekhe [21], which also relies in the displacement of MSA with a non-solvent).

Both chloroform and methanol are highly volatile, while MSA is not; hence MSA needs to be removed from the resulting BBL NW suspension prior to casting films, otherwise MSA would re-dissolve NWs during casting. Therefore, BBL NW suspensions were centrifuged for 10 min at ≈910 g to make NWs settle to the bottom of a phial. Clear excess solvent was carefully pipetted off from above the settled NWs, before being replenished with either methanol, ethanol, or isopropanol; BBL NWs dispersed well in alcohols, and we later did not find any systematic differences in the electrical behaviour of BBL nanobelt films cast from either dispersion agent. BBL NWs did not disperse in water though, so we could not prepare aqueous BBL NW formulations. This process was then repeated three times. Eventually, this resulted in BBL NWs suspended in clear carrier solvent almost free of MSA, and with no residual dissolved BBL that has not been incorporated into NWs.

2.2. NW TFT preparation

We prepared OSC NWs onto Au electrode pairs of width $W = 2$ mm, separated by a channel of length $L = 10$ μm (for P3HT samples), and of length 20 μm for BBL samples, to account for the larger size of BBL nanobelts, giving ratios $W/L = 200$ for P3HT; $W/L = 100$ for BBL. 100 nm thick gold contacts were prepared by photolithography onto insulating SiO_2 substrates after depositing 10 nm of Cr as adhesion layer. The contact geometry, sketched in Fig. 1, uses 0.1 mm thin wires to connect S/D contacts to distant contact pads. This design limits overlap area between Au con-