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Comparing electron- and hole transporting semiconductors in ion sensitive water- gated transistors

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ABSTRACT

We present a systematic study comparing different solution-processed semiconductors in cation- sensitive water-gated thin film transistors (WGTFTs): A hole transporting semiconducting polymer (rrP3HT), and an electron-transporting precursor- route metal oxide (ZnO). To allow comparison, we used the same ionophore to sensitise the gate contact for both semiconductors. We find both organic hole transporter and inorganic electron transporter have their relative merits, and drawbacks, in ion- sensitive WGTFTs. Hole transporting rrP3HT WGTFTs show low hysteresis under water- gating and give super- Nernstian sensitivity. However, rrP3HT responds to ionic strength in water even when WGTFTs are not sensitised, compromising selectivity. Electron transporting ZnO WGTFTs show higher mobility, but also stronger hysteresis, and sub- Nernstian response. However, ZnO WGTFTs show little response to ionic strength when not sensitised. We rationalise the super- versus- sub-Nernstian sensitivities via a capacitive amplification/attenuation effect. Our study suggests that the optimum semiconductor material for ion- selective WGTFTs would be a precursor- route inorganic hole transporting semiconductor.

1. Introduction

The discovery of Kergoat et al. [1] that organic thin film transistors (OTFTs) can be gated using water as an electrolytic gate medium has opened the possibility of using such devices as transducers for the sensing of waterborne analytes. In contrast to the classic ion- sensitive field effect transistor (ISFET [2]), here the sample itself is an active part of the transducer. A number of workers have since demonstrated 'water- gated thin film transistor' (WGTFT) sensors for biologically relevant molecules [3–6], pH [7], and specific cations [8–10], usually by introducing analyte-specific receptors ('sensitisers') into the WGTFT architecture. To sensitise for cations, cation selective 'ionophores' were used, e.g. calixarenes [8–10], or valinomycin [9]. The ionophore was introduced similarly as in conventional electrochemical (potentiometric) cation sensors [e.g. 11,12], namely, by including a plasticised PVC membrane with embedded ionophore in the WGTFT [8,9], or alternatively, dispersed within an organic semiconductor film [10,13]. The threshold of ionophore- sensitised WGTFTs shifted as a result of an ion concentration dependent membrane potential with characteristics logarithmic in ion concentration, similar to Nernstian (more precisely, Nikolsky- Eisenman) characteristics observed in potentiometric ion sensors.

As an alternative to organic semiconductors, solution- processed precursor route inorganic semiconductors have recently gained popularity, as they can be processed with similar ease. Precursors may be metal acetates, chlorides, or nitrates, processed by spin casting and later pyrolysis, or spraying directly onto hot substrates (spray pyrolysis) from solutions in polar solvents or water. Pyrolysis converts such precursors into semiconducting oxides such as ZnO, SnO_2, TiO_2, IGZO or In_2O_3 [14–18]. These metal oxides lead to electron- transporting TFTs, while water- gated organic TFTs usually are hole- transporting. ZnO- based devices in particular have recently been widely used in various sensor devices [19–22].

We present here a systematic study comparing cation- sensitive WGTFTs using either, a hole transporting semiconducting polymer (rrP3HT), or an electron- transporting precursor- route metal oxide (ZnO), as the semiconductor. In both cases, we used a simplified WGTFT architecture, similar as Melzer et al. [9], where the ion- selective membrane was prepared on the gate electrode and analyte solution is used as the gate medium. In the original report on WGTFT ion sensors, List- Kratochvil et al. [8], had instead used a more complicated two- chamber system where a free-standing membrane separated the analyte from a reference solution, with gating by the reference solution. As ionophore, we used water-insoluble dibenzo crown ether (Dibenzo-

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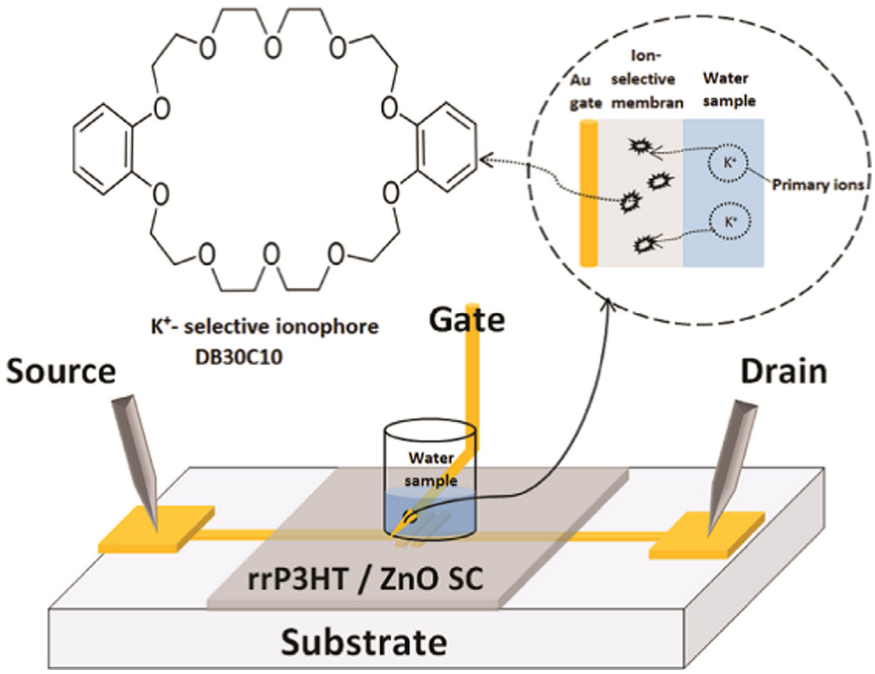

Fig. 1. Design of K^+ sensitive water- gated TFT. Au gate needle sensitised with DB30C10 ionophore embedded in a plasticised PVC membrane. The ionophore's molecular structure is shown in the inset.

30-crown-10, DB30C10, inset Fig. 1) [23,24]. DB30C10 has previously shown sensitivity for potassium [25] and selectivity over sodium (selectivity constant 117) as established by the equipotential method in mixed Na^+/K^+ solutions in a potentiometric ion sensor [26], but so far crown ethers have not been introduced into ion- sensitive WGTFTs.

2. Experimental

Transistor substrates were prepared by shadow mask evaporation of Au source/drain contact pairs with Cr adhesion layer (contact width W = 1 mm separated by an L = 30 µm channel; W/L = 33.3) onto clean glass substrates. The hole transporting semiconducting polymer regioregular poly(3-hexyl)thiophene (rrP3HT) was purchased from Aldrich (Cat No 698989, electronic grade 99.995% trace metal basis), dissolved at 4 mg/mL in toluene solution, heated gently at 75 °C for ≈ 10 min, and spin cast onto contact substrates at 2000 rpm for 60 s. After casting, films were dried under dynamic vacuum at 120 °C for 1 h. The semicrystalline morphology of rrP3HT films used in sensors has been studied in detail before, e.g. [27–29]. Zinc oxide films were prepared by spraying 3 'puffs' of 100 mM $ZnCl_2$ solution in DI water onto similar TFT substrates heated to 400 °C on a hotplate, which leads to the formation of semiconducting ZnO films('spray pyrolysis', more processing details in [30]). Film thickness was determined with a Veeco Dektak XT surface contact profilometer as 15 nm for rrP3HT and 80 nm for ZnO; ZnO films also are significantly rougher. This agrees with the report of Lehraki *et al.* [31] who showed that spray pyrolysis from zinc chloride precursor leads to highest crystallinity (compared to acetate and nitrate) with largest crystals. This promises higher carrier mobility, but also leads to rougher films and the need for higher thickness to ensure continuity. After spraying, films were first cleaned by DI water, isopropanol, acetone, and UV ozone. Then, ZnO films were treated with hexamethyldisilazane (HMDS) to passivate their amphoteric surface. This was by spraying ~ 1 mL of HMDS into the air inlet of a pre-heated (80 °C) and previously evacuated vacuum oven and keeping films in this atmosphere for 2 h. A goniometer tensiometer coupled with Attension Theta software package was used to determine contact angles of deionized water on rrP3HT and ZnO films.

To prepare K^+ selective membranes, we mixed PVC membrane cocktails from 1.3% of potassium tetrakis [4-chlorophenyl]borate salt, 3.1% 2,3,17,18-Dibenzo-1,4,7,10,13,16,19,22,25,28-decaoxacyclotriaconta-2,17-diene ('DB30C10', Aldrich Cat No 332518) ionophore, 30% poly(vinyl chloride) (PVC), and 65.6% 2-Nitrophenyl octyl ether as plasticiser, similar as in [9]. In total 100 mg of membrane components were dissolved in 3.5 mL of tetrahydrofuran (THF). An L- shaped Au needle was immersed in this solution for several hours, and then dried overnight. In accordance with common practice [e.g. 9, 11], Coated needles were pre-conditioned in 1 mM KCl for several hours. Introducing the ion-sensitive membrane as a coating on the gate needle rather than as a free-standing layer was introduced by Melzer *et al.* [9] for a different ionophore. Aqueous cation solutions were prepared by dissolving KCl or NaCl in deionised (DI) water to a concentration of 100 mM and repeatedly diluted to prepare sample solutions down to 1 nM. Transistors were completed using aqueous cation solutions as electrolytic gate media, starting at the lowest concentration (1 nM) and successively replacing them with solutions of increasing concentration. Electrolyte solutions were held in a small plastic pool of 50 µL capacity that was mounted over the TFT substrate's channel area, as described previously [10]. The solution in the pool was contacted with L- shaped Au needles overlapping the channel along its width to act as a gate contact. Fig. 1 illustrates the resulting WGTFT architecture. To reach equilibrium, we allowed 2 min exposure to electrolyte before each electrical measurement. Then, we recorded transfer characteristics by measuring drain current I_D at drain voltage, $V_D = -0.1$ V for rrP3HT TFTs (+0.1 V for ZnO TFTs), while sweeping gate voltage V_G at 10 mV/s from + 0.2 V to − 0.7 V, and back to + 0.2 V for rrP3HT TFTs (from −0.2 V to +0.7 V and back to −0.2 V for ZnO TFTs). We limited voltage sweeps to 0.7 V rather than the full 'electrochemical window' of water of 1.23 V because it was shown previously that rrP3HT long-term stability may be compromised at higher voltages [8]. Results are presented on a linear drain current (I_D) scale, and 'master curves' were constructed by shifting transfer characteristics along the gate voltage axis until they best matched with the 1 nM characteristic. Carrier mobility was evaluated from master curves with standard transistor equations, assuming a capacitance of 3 µF/cm^2 [1]. The required shift along the gate voltage axis was taken as the threshold shift under respective ion concentration and was fitted to the Nikolsky- Eisenman