Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Solution Processed Liquid Metal – Conducting Polymer Hybrid Thin Films in Electrochemical pH -Threshold Indicators

Evangelia Mitraka, Loig Kergoat, Zia Ullah Khan, Simone Fabiano, Olivier Douhéret, Philippe Leclère, Marie Nilsson, Peter Andersson Ersman, Göran Gustafsson, Roberto Lazzaroni, Magnus Berggren and Xavier Crispin*

xavier.crispin@liu.se

Experimental Section

Film manufacturing/Synthesis: The GaInSn-PEDOT:Tos films were prepared using the following materials: iron (III) tris-p-toluenesulphonate (40wt%) in butanol (Clevios™ CB 40 V2), anhydrous pyridine (Aldrich), the liquid metal alloy GaInSn (MCP-11 by MCP Ltd Wellingborough) of composition (66% Ga, 20.5% In, 13.5% Sn) and 3,4-Ethylenedioxythiophene (Sigma-Aldrich).

The chemical polymerization of EDOT in the presence of iron tosylate followed a method described elsewhere.[1] Pyridine is added in the Clevios™ solution (0.5 mol per 1 mol of iron tosylate) as an inhibitor to control the kinetics of the polymerization. The solution is stirred for 2 hours before GaInSn is added. GaInSn gets dispersed in the solution using an ultrasonic gun (Sonopuls HD2200 by Bandelin). Extra attention is given to the solution not to increase its temperature due to the sonication. When the alloy is completely dispersed, EDOT is added and the solution is stirred in a vortex mixer (VWR). The resulting solution is spin coated on the substrate (500rpm for 5sec and 1500rpm for 10sec) and baked on a hot-plate at 90^{o}C for 30min to complete the polymerization. The obtained film thickness is ca. 350-400nm in PEDOT:Tos areas, while it can be up to the microscale where GaInSn is present, as measured with a DEKTAK profilometer. Finally, the GaInSn-PEDOT:Tos films are rinsed in n-butanol, in order to remove the excess of iron, and subsequently dried with nitrogen.

Morphology Study: The morphology of the hybrid films was studied both by Scanning Electron Microscopy (SEM) and Atomic Force Microscopy (AFM). The SEM experiments were conducted by using a Hitachi SU8010 FE-SEM microscope. The AFM experiments were carried out with a Bruker ICON microscope operating in ambient conditions in peak-force tapping mode. They were monitored with a Nanoscope V Controller. The etched Si probes used were purchased for Nanosensors GmbH (Ref. PPP-NCHR).

Thickness Measurement: The thickness of each individual film was measured by using a surface profilometer Dektak 3ST by Veeco. A part of the film is scratched in order to have a film-free substrate area. Then, the tip, starting from a point on the film, crosses through the film-free area and it gets on the film again. Thus, both the surface profile and the film thickness are recorded. The force applied to the tip is 4mg and the thickness range is 655 kÅ. The distance that the tip scans can vary from 4 to 10mm.

Resistance-Conductivity Measurement: The resistance of the GaInSn-PEDOT:Tos films was measured with four-point probes method using a Keithley 4200. The applied voltage was up to 10^{-4} V with a step of 10^{-5}V. The conductivity of the films was then calculated as $\sigma = L/(R \cdot A)$, where L is the distance between the golden electrodes (0.98cm), A is the cross sectional area of the sample (the thickness multiplied with the width ~6mm) and R is the resistance which was measured.

Spectrophotometry Study: The optical properties of the samples after acidic and basic treatment were studied in the UV/Vis/NIR range using a spectrophotometer PerkinElmer Lambda 900.

Open Circuit Potential and Transistor Configuration: The GaInSn-PEDOT:Tos composite film was used as the working electrode and it was spin coated on plastic foil, while the counter electrode consists of PEDOT-PSS. Moreover, the source, the drain and the channel of the transistors are screen printed on plastic foils. The source and the drain consist of a carbon conductive composition **(**DuPont 7102**)**. The channel (100μm in length) which connects the source with the drain (Figure 5a left) was made of PEDOT-PSS. An insulator covers the source and partially the channel in the transistor used in Figure 5e, while the insulator covers the source and drain and partially the channel in the transistor used in Figure 5c. A hole in the insulator permits the gate to come in contact with the channel. However, the gate electrode addresses the transistor channel via an electrolyte (poly[sodium 4-styrenesulfonate], PSSNa), not through direct contact, and thus induces electrochemistry to occur in the channel. The pristine state of PEDOT-PSS is highly p-doped and conducting. Therefore, modulation of the current flowing through the channel (I_{DS}) can be achieved by de-doping the PEDOT-PSS electrochemically.

The open circuit potential (V_{oc}) between the GaInSn-PEDOT:Tos film and the PEDOT-PSS film was measured using a Keithley 2602A. This voltage was applied to the gate of an electrochemical transistor, through a probe. Only when the voltage (V_{oc}) achieved its maximum, the probe was connected to the gate. The modulation of the drain current (I_{DS}) was recorded by a Keithley 2612B.

Droplet Size Distribution

By analyzing the SEM images at various magnifications, it is possible to estimate the particle size distribution (**Figure S1**). This follows a power law distribution over approximately four orders of magnitude, with a high concentration of smaller particles in the film. The evolution follows the relation:

$$\log(N) = 8 - 2.142 \cdot \log(d)$$

where N is the number of droplets, and d is the diameter (in nm). The slope (D) of the best fit line is 2.142 and according to the literature [2] when D~2.0 it means that the lowest particle size that fits the trendline (in our case ~ 35nm) corresponds to fragments which are not undergoing substantial comminution. In other words, a slope of D~2.0 means that small particles are volumetrically more rear and hence poorly comminuted, since stresses are concentrated at the contact points between large particles. Therefore, the higher the D value, the finer the particles. In our case D is ca. 2.0 confirming our particle size distribution estimation, where the particles with a diameter of 35-40 nm seem to be the majority on the film, whereas below that size the number of particles decreases. However, it is difficult to be precise on the number of particles,[3] especially in sizes below 20 nm, since they can be hidden by the PEDOT film, which acts as a shell above and in between the droplets.

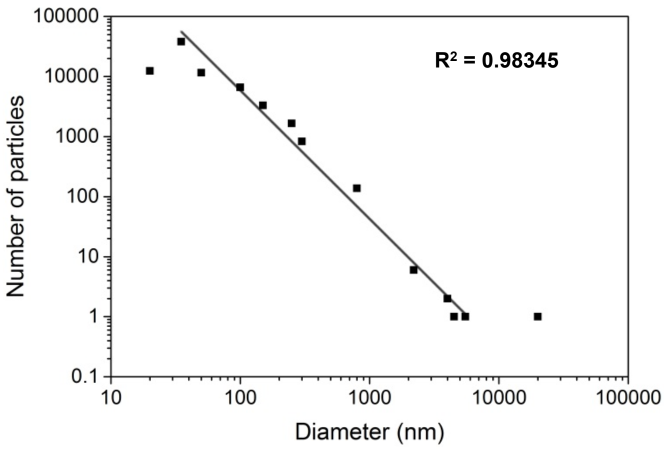

Figure S1. Estimation of the droplet size distribution on a GaInSn-PEDOT:Tos film.

AFM and C-AFM images of plain PEDOT:Tos

Figure S2 presents (a) the height and (b) current images of a PEDOT:Tos layer. The left image presents PEDOT:Tos covering a bare glass substrate with an ITO electrode (on the right side of the image) and reveals the homogeneity of the film despite the strong topographical contrast (height difference about 400 nm). The C-AFM image of PEDOT:Tos (on the right side) confirms the homogeneous layers of the polymer and its high, uniform conductivity.

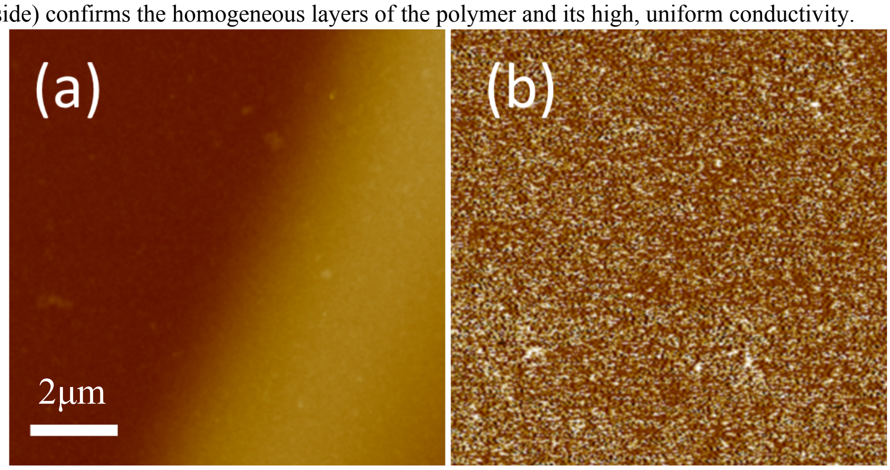

Figure S2. (a) Topographic image of a thin PEDOT:Tos layer on ITO electrode and glass (Z range 400 nm) (b) corresponding current image (Current range 25 pA).

Thickness Measurement

The morphology of the GaInSn-PEDOT:Tos films is unique and quite rough in the nanoscale. Small and bigger GaInSn droplets blended with the conducting polymer forming a network with several levels. Consequently, the surface profile of the film appears to have many peaks and valleys, as shown in **Figure S3**. This makes the thickness measurement challenging. The spikes are due to GaInSn droplets, while the cliffs are probably areas of polymer in between the droplets.

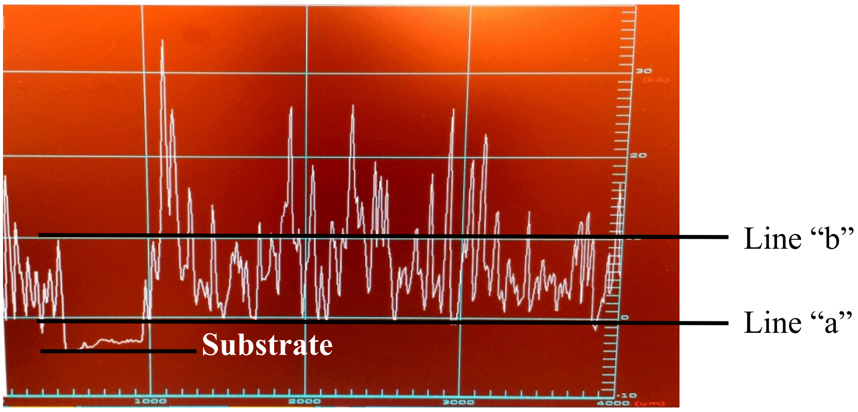

Figure S3. Surface profile of a GaInSn-PEDOT:Tos film.

Since it is difficult to define the thickness of the film, the conductivity was calculated twice. Once for the polymer areas in between the droplets (Line “a”) and once for the average GaInSn droplet size (Line “b”). We thought that the high spikes, possibly corresponding to bigger droplets, should not be considered for the thickness, since they are not representative of the film.

Discussion on the Mechanism of PEDOT:Tos Reduction after Acidic Treatment

The reduction mechanism of the GaInSn-PEDOT:Tos film after acidic treatment is not completely clarified. However, we carried out some fundamental experiments, in both ambient and controlled conditions (glovebox). In both conditions, a pure PEDOT:Tos film was drop casted with just a single GaInSn droplet. It was observed that in both cases the conducting polymer maintained its oxidized state. When the same procedure was repeated using a GaInSn droplet treated with HCl, it was observed that in ambient conditions the PEDOT:Tos film gets reduced (turns blue, indicating its neutral state). On the other hand, in the glovebox, when an HCl treated droplet was drop casted on the conducting polymer, the film remained in its oxidized state. It worth mentioning that in the experiment taking place in the glovebox, the treated GaInSn droplet was left for a few minutes in the N_2 environment to dry from H_2O formed on its surface due to the reaction of Ga_2O_3 with HCl. The droplet was then dropcasted.

Therefore, considering these facts, one shall suggest that the reduction mechanism involves the motion of electrons from the bulk of the liquid metal droplet, however, only in presence of water (or even moisture). Herein we present some possible reactions that take place consecutively:

Oxide skin: $Ga_2O_3 + 6HCl \rightarrow 2GaCl_3 + 3H_2O$

$Ga_2O + 6HCl \rightarrow 2GaCl_3 + H_2O + 4H^+ + 4e^-$

Droplet Bulk: $In^0 + 3HCl \rightarrow InCl_3 + 3H^+ + 3e^-$

Matrix: $PEDOT^+{:}Tos^- + e^- \rightarrow PEDOT^0 + Tos^-$

Dependence of Conductivity over Basic pH

The conductivity data vs pH for plain PEDOT:Tos and GaInSn-PEDOT:Tos films is presented in Figure S4a. A slight decrease of conductivity is observed in pH>10 for the plain PEDOT:Tos films while this decrease is very abrupt for the hybrid films. This steep decrease in conductivity at high pH for the hybrid films is due to the amphoterism of gallium oxide which is the main component of the oxide skin of GaInSn. Thus the oxide skin can react as an acid as well as a base. The conductivity drop above pH=10 is also accompanied with a dramatic change in the absorption spectrum (Figure S4b). Upon increasing the pH (from pH=7 to 13) leads to a lowering of the signal at 900 nm and the appearance of a new absorption peak at 580 nm originating from neutral $PEDOT^0$ segments. However, the focus of this manuscript is on the behavior of those composites on low pH side because PEDOT:Tos deteriotates at high pH and lead to unreliable devices.

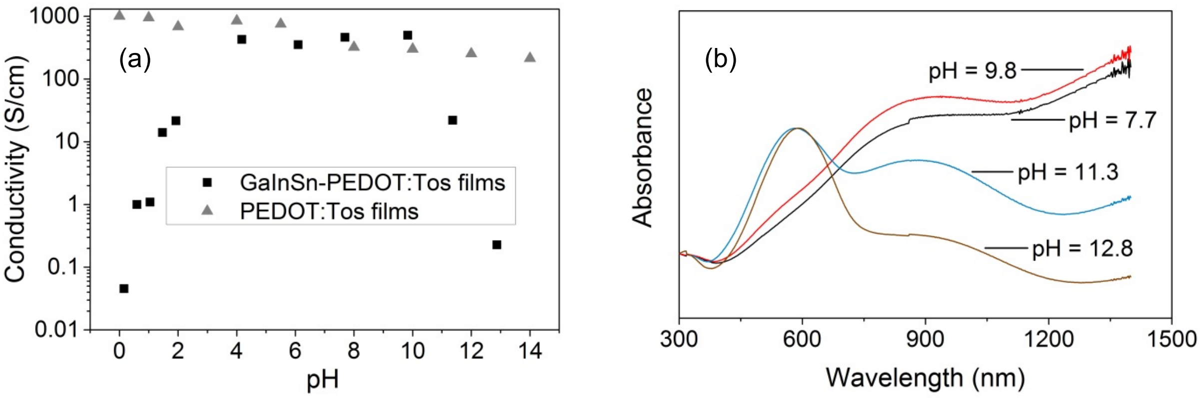

Figure S4. (a) Conductivity of the GaInSn-PEDOT:Tos films and plain PEDOT:Tos films after treatment in solutions at different pH (the conductivities of the GaInSn-PEDOT:Tos films presented here are calculated using the thickness corresponding to Line "a" of Figure S3), (b) Absorption spectra of GaInSn-PEDOT:Tos films after treatment in aqueous solutions with pH > 7.7.

PEDOT work function dependence on pH

In Figure S5 we present the secondary electron cut-off in a ultra-violet photoemission spectra (HeI=21.2eV) for a PEDOT:Tos film after pH treatment. We observe no clear trend in the work function changes (WF varies between 4.38-4.6eV for the acidic range), but what is clear is that whetever the pH value, the PEDOT:Tos has always a higher work function than GaInSn, confirming the electron transfer is from GaInSn to PEDOT.

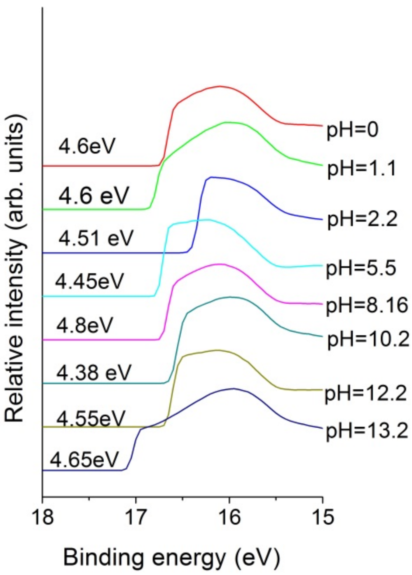

Figure S5. PEDOT work function dependency with pH.

Open Circuit Voltage and Drain Current Modulation over basic pH

The V_{oc} and the I_{DS} modulation over basic pH for the same set of transistor accompanied with the same sensing electrodes are presented in Figure S6. It is observed that the V_{oc} obtained by the two electrodes reaches 0.6V for pH=13.2. When this V_{oc} is applied on the gate of the transistor, it does not result in high I_{DS} modulation, which in turn implies that the detection area of this transistor is mainly at low pH.

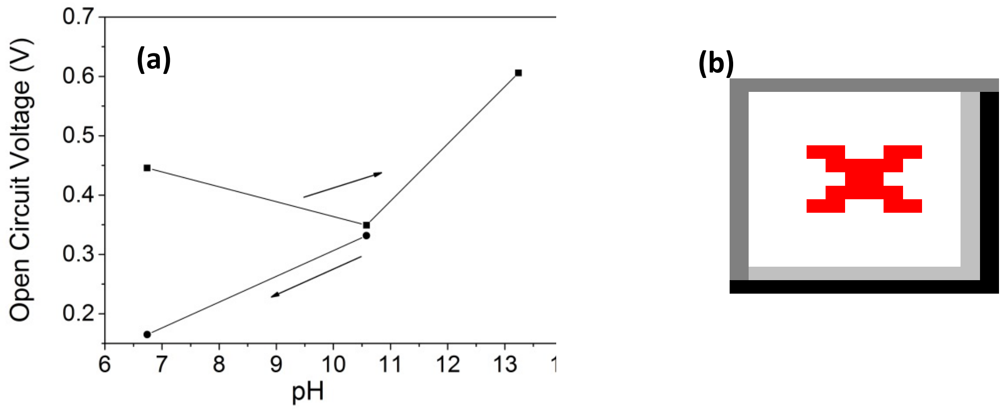

Figure S6. (a) The V_{oc} measured when the same set of electrodes were immersed sequentially from pH=7 to pH=13.2 and back to pH=7. (b) The modulation of the OECT drain current (I_{DS}) when the V_{oc} of Figure S6a is applied on the gate. The same transistor that corresponds to the measurement shown in Figure 5c was used throughout this experiment.

1 B. Winther-Jensen, D. W. Breiby, K. West, *Synth. Met.*, 2005, **152**, 1.
2 A. Billi, *J. Struct. Geol.*, 2007, **29**, 1512.
3 S. M. Zielinski, A. a. Sansone, M. Ziolkowski, R. P. Taleyarkhan, *J. Heat Transfer* , 2011, **133,** 071201.