ADVANCED ELECTRONIC MATERIALS

Supporting Information

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Low-Temperature Processing of Printed Field-Effect
Transistors from Sublimating-Stabilizer Derived Oxide
Nanodispersions

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A. Agglomerate size comparison of camphor and thymol stabilized In_2O_3 nanoinks

Among various possible aromatic compounds/ molecules that can be used as low temperature sublimating stabilizers, camphor and thymol have been chosen based on their low sublimation temperature (for example, for camphor it is 0-25 °C and thymol 0-40 °C), absence of toxicity (both used as food additives in industries), low cost and potential for stable nanoink formation. Among these thymol is used as pharmaceutical stabilizer and anticipated to be a better stabilizer due to the presence of hydroxyl group. Accordingly, the dynamic light scattering (DLS) measurements (Figure S1) performed on nanoinks prepared from camphor and thymol stabilized In_2O_3 nanoparticles show a stable (shelf life of about 2 weeks) and printable dispersion for thymol stabilized ink, whereas the camphor based dispersions turned out to be unstable (settling down within short time) and have large size agglomerates making it unsuitable for inkjet printing. Consequently, further studies have been carried out on thymol stabilized inks only.

Figure S1: Dynamic light scattering of camphor and thymol stabilized In_2O_3 nanoinks

B. Time stability of thymol stabilized nanoink

Figure S2: Time stability of thymol stabilized In_2O_3 nanoink dispersed/ milled for 180 minutes

C. Additional electrical characterization data

After printing the semiconducting nanoparticle layers on the FET device structure bridging the drain/ source electrodes, the drain-source currents were recorded by applying a small drain voltage, before and after the heating routine (100 °C, on hot plate) performed on the printed nanoparticulate layer. These results refer to batch A of the semiconductor inks, where one-step heating was performed after printing. The I-V measurement results are shown in Figure S3. While, the layers after heating on the hotplate show completely Ohmic transport behaviour, the current-voltage characteristics prior the annealing routine (that is when thymol molecules are present at the particle surface/ interface) is quite different. The non-Ohmic behaviour somewhat resembles the forward bias transport in tunnel diodes.

Figure S3: Two probe current-voltage measurements of the printed semiconducting In_2O_3 nanoparticle channel FETs showing the effectiveness of the short heating routine to sublimate and remove the thymol molecules that stabilizes the nanoparticulate inks; each black and red line in the figure is from an individual device before and after the heating step.

D. X-ray diffraction pattern of different In₂O₃ nanoparticles, used for nanoink preparation

Two different batches of commercially available semiconducting In₂O₃ nanoparticles have been used in this study to prepare the nanodispersions; the smaller particles were purchased from Plasmachem GmbH and the larger ones from Iolitech GmbH. Here, the X-ray diffraction (XRD) measurements were carried out to probe the average primary particle size in each case (Figure S4). The reflections of the XRD patterns are indexed and compared with the Inorganic Crystal Structure Database (ICSD) to confirm phase-pure In₂O₃ in either case. The average crystallite size was estimated using Debye-Scherrer equation S1, which resulted in a size of about 24 nm and 72 nm for the smaller and bigger nanoparticles, respectively.

$$t = \frac{0.9 \lambda}{\beta \cos \theta} \quad (\text{S1})$$

where t , λ and β correspond to the average crystallite size, the wavelength of the radiation and the diffraction peak position in radian, respectively.

Figure S4: XRD of the commercially available semiconducting In₂O₃ nanoparticles from two different sources

E. Atomic force microscopy (AFM) images showing the surface topography of the printed In_2O_3 nanoparticulate films

Atomic force microscopy has been carried out using Bruker dimension icon atomic force microscope (tapping mode). The representative images shown in Figure S7 reveal the surface topography of printed In_2O_3 nanoparticulate film using nanoinks that has been dispersed/ milled for 300 minutes. The dimension of the printed area/ layer has been identical to the real device. The RMS surface roughness values for the $1 \times 1 \mu\text{m}^2$ frame (a) and $2 \times 2 \mu\text{m}^2$ frame (b) turn out to be 11.2 nm and 13.9 nm, respectively.

Figure S5: AFM images of typical printed area of In_2O_3 nanoink with different frame size (a) $1 \times 1 \mu\text{m}^2$ and (b) $2 \times 2 \mu\text{m}^2$.

F. Cross-section scanning electron microscopy of the printed In_2O_3 nanoparticulate layer and composite solid polymer electrolyte interface

Representative cross-section SEM image showing the In_2O_3 nanoparticulate semiconductor/ electrolyte interface; the dimension of the printed area/ layer has been identical to the real device.

Figure S6: Cross-section SEM images of the semiconductor channel-electrolyte interface, where the semiconducting In_2O_3 nanoink has been milled/ dispersed for 300 minutes.

G. Transmission electron microscopy (TEM) and scanning transmission electron microscopy (STEM) image of the printed In_2O_3 -solid polymer electrolyte layer interface

Figure S7: (a) TEM and (b) STEM image showing the In_2O_3 channel/solid polymer electrolyte interface; the deposited platinum during FIB sample preparation can be seen on top of the electrolyte layer.

H. Energy dispersive X-ray spectroscopy (EDX) elemental mapping of the In_2O_3 channel/ solid polymer electrolyte interface

Figure S8: (a) and (b) show the EDX elemental (In, C and Pt) mapping of the semiconductor electrolyte interface. The carbon mapping clearly shows the In_2O_3 -electrolyte boundary. The weak presence of carbon signal at the Pt and In_2O_3 layer can be due to natural contamination of hydrocarbon from air or during thinning of the cross-section sample with Ga ion beam (FIB sample preparation).

I. EDX elemental line mapping of the printed semiconductor-electrolyte interface

Figure S9: The elemental line map shows the distribution of In, C and platinum across that deposited platinum-solid polymer electrolyte-In₂O₃ layers.

J. Estimation of double-layer capacitance (C_{DL}) from the displacement current measurement on the FET device

Figure S10: (a) Variation of gate current with applied gate voltage with different gate voltage scan rates (b) Saturation gate current vs. scan rates; slope of which gives the capacitance of the semiconductor channel.

The double layer capacitance (C_{DL}) has been calculated as follows:

$$Q = CV$$

Differentiating we get,

$$\frac{dQ}{dt} = C \frac{dV}{dt} \text{ when } C \text{ is constant.}$$

or, $i = Cv$ when C is constant.

Therefore, from the saturation current part of the I_G versus V_G plot, one can determine the capacitance from the slope of the i versus v plot.

Following this, the double layer capacitance (C_{DL}) has been estimated to be $C_{DL} = 4.7 \mu F/cm^2$.

K. Scanning electron microscopy images of In_2O_3 nanoinks that are dispersed/ de-agglomerated for different timescale.

Figure S11: FESEM images of inkjet printed In_2O_3 nanoparticulate films prepared from nanoinks that have been de-agglomerated/ dispersed or milled for (a) 90 minutes, (b) 180 minutes and (c) 300 minutes, respectively.

L. Contact angle measurements

The contact angle measurements were performed using Holmarc Contact Angle Meter. The contact angle of the composite solid polymer electrolyte is compared with the contact angle of pure solvent, DMSO. The contact angle measurement was carried out on the ITO coated glass substrate used for device fabrication, where the ITO has been structured to serve as the device electrodes.

Figure S12: The contact angle of (a) DMSO and (b) the composite solid polymer electrolyte on ITO coated glass substrate.

M. Representative optical microscopy image of the inkjet-printed FET device

Figure S13: Representative optical microscopy image of an inkjet-printed electrolyte-gated MOSFET; the nanoink bridges the channel, while the electrolyte is printed in a way to cover most of the gate area and having least-possible overlap with the electrodes, in order to ensure low parasitic capacitance.

N. Transfer and output characteristics of an archetypal FET device fabricated using the bigger In_2O_3 nanoparticle based nanoink

The transfer and output characteristics of an exemplary FET device fabricated from nanoinks of the bigger In_2O_3 nanoparticles are shown in Figure S14. Here, the average on-currents ($I_{\text{D,ON}} = 160 \mu\text{A}$) and device mobility ($\mu_{\text{FET}} = 4.3 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$) values have not been as large as has been obtained from the nanoinks consisting of smaller primary particles. The reason behind this counter intuitive observation (bigger particles should cause less inter-particle scattering and high mobility) is again the inferior quality of the nanodispersion itself (also have shown lower shelf-life), however, due to the larger primary particle size the NDR effect has been absent.

Figure S14: Archetypal transfer and output characteristics of FETs made from thymol stabilized nanodispersions of bigger In_2O_3 nanoparticles with 180 minutes of Dispermat milling time. The FET channel has been printed with three layers of nanoinks with intermediate heating at 100°C .

O. Transfer and output characteristics of typical FET device from smaller In_2O_3 nanoparticle based nanoinks and without removal of surfactant (thymol) molecules

Figure S15: Transfer and output characteristics of FETs prepared with nanoinks from smaller nanoparticles and inks that are dispersed/ milled for 300 minutes; however, in this case, the annealing step has been omitted, i.e., the electrolytic insulator has been printed directly onto as-printed nanoparticles with thymol at the particle surface/ interface.

Average mobility [$\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$]	Average transconductance [$\mu\text{S } \mu\text{m}^{-1}$]	Average On-current [μA]	Average On/Off
1.06 ± 0.03	0.75 ± 0.1	24.7 ± 2.2	$(4 \pm 0.9) \times 10^6$