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Stable crosslinked gate electrodes for hygroscopic insulator OTFT sensors

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Hydration of GOPS crosslinked device: before and after

GOPS crosslinking requires high temperatures (140°C for 30 minutes), which has the effect of drying out the HIFET and losing transistor characteristics at low voltage. Figure S1 below shows the characteristics of an example HIFET with a GOPS crosslinked gate electrode before and after hydration with deionised water.

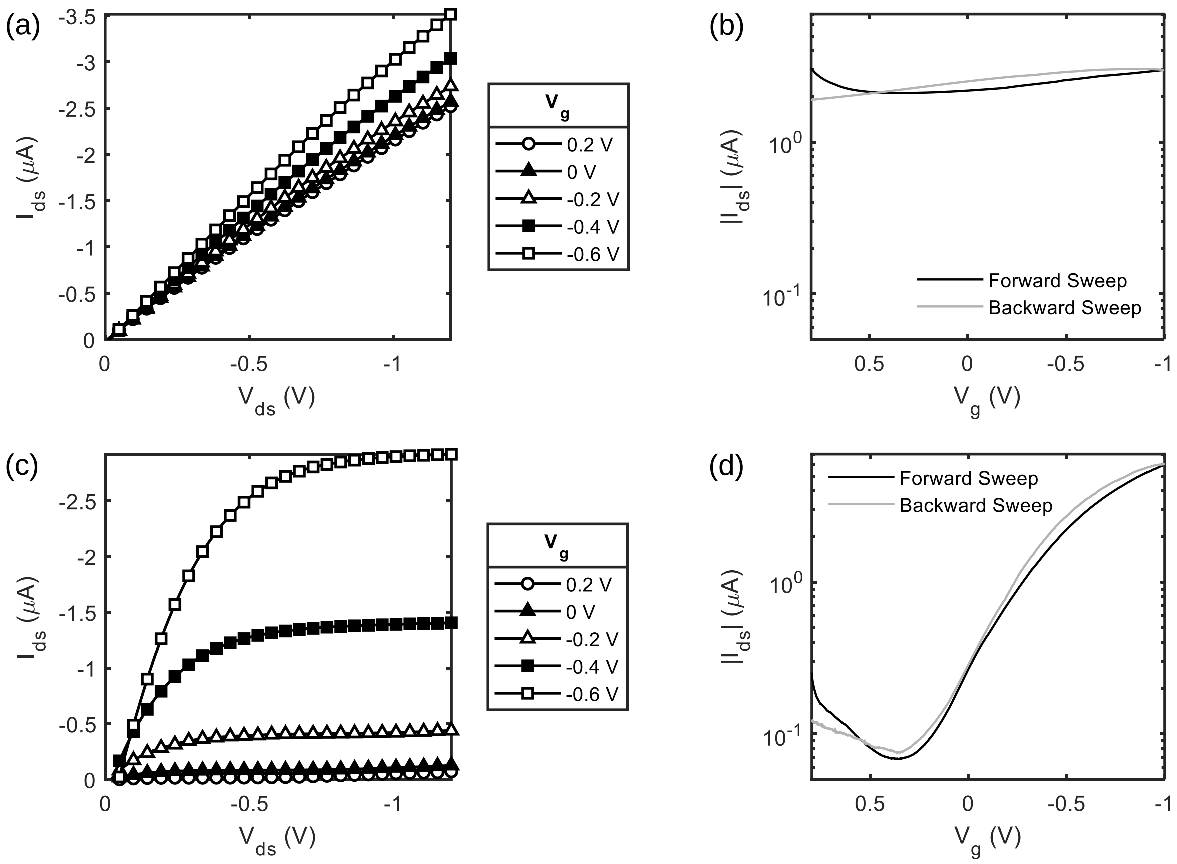

Figure S1 | Output and transfer characteristics for the same device before (a,b) and after (c,d) hydration with 5 μL of deionised water.

Gate conductance analysis from IV characteristics

Gate conductance was estimated by taking the average gradient of linear regressions fitted to IV sweeps between +1 V and -1 V for each sample. 6 samples of each gate type were tested. Data was collected by sweeping forwards and backwards, but no significant hysteresis was observed when dry. All measurements are shown in Figure S2 below, and the most representative data (closest to average) for each type is plotted together for comparison in Figure 4a of the main text. Table S1 lists the average conductance and standard deviation for each gate type, along with film thicknesses and estimated conductivities. Thickness measurements were taken toward the centre of the film, and so does not take into account the thickening of the film near the edges (a by-product of the drop casting method), which appeared to be most significant for the DVS samples. This may result in an underestimate of the average cross-section, and hence an overestimation of the conductivity.

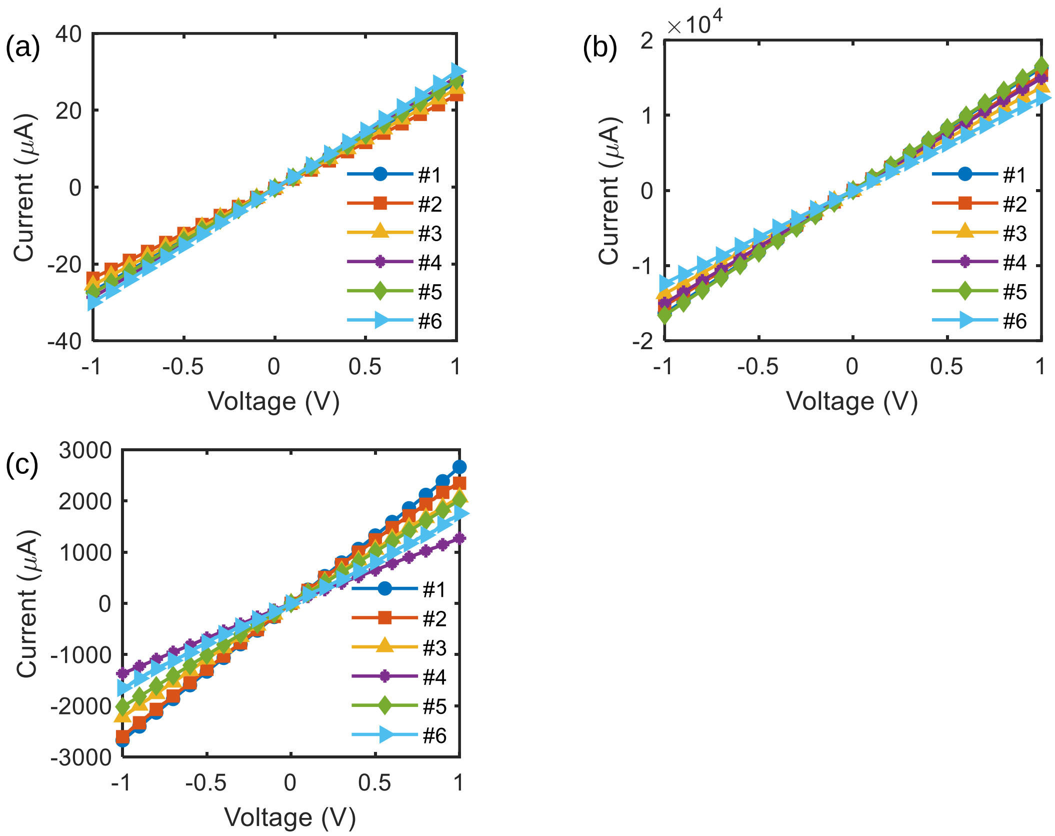

Figure S2 | IV sweeps for (a) the standard gate electrode, (b) DVS crosslinked gate electrodes, and (c) GOPS crosslinked gate electrodes.

Table S1 | Tabulated average thickness, conductance and conductivity of each gate type. Conductivities are calculated from thickness and conductance values, assuming a constant thickness.

Gate type	Thickness (μm)	Conductance (μS)	Conductivity (S m^{-1})
Standard	3.6±0.4	27±2	11±1
DVS crosslinked	1.0±0.2	14,900±1,600	22,400±5,500
GOPS crosslinked	2.5±0.4	2,080±520	1,230±360

DVS crosslinked gate electrodes – *in-situ* trial

Figure S3 shows the characteristics of a HIFET with a gate electrode of DVS crosslinked PEDOT:PSS (without ethylene glycol and DBSA), deposited and dried *in-situ*. The device fails to exhibit transistor functionality, instead functioning as a resistor with a current depending on the gate-drain voltage. The size of the gate current during the transfer sweep (Figure S3c) indicates significant gate-to-channel leakage, suggesting that insulating layer had been severely damaged as a result of contact with the DVS/PEDOT:PSS solution. This led us to the *ex-situ* DVS crosslinking method (crosslinking is done separately and the freestanding film is transferred onto the transistor), and to the alternative GOPS crosslinking method, which is far less damaging than DVS.

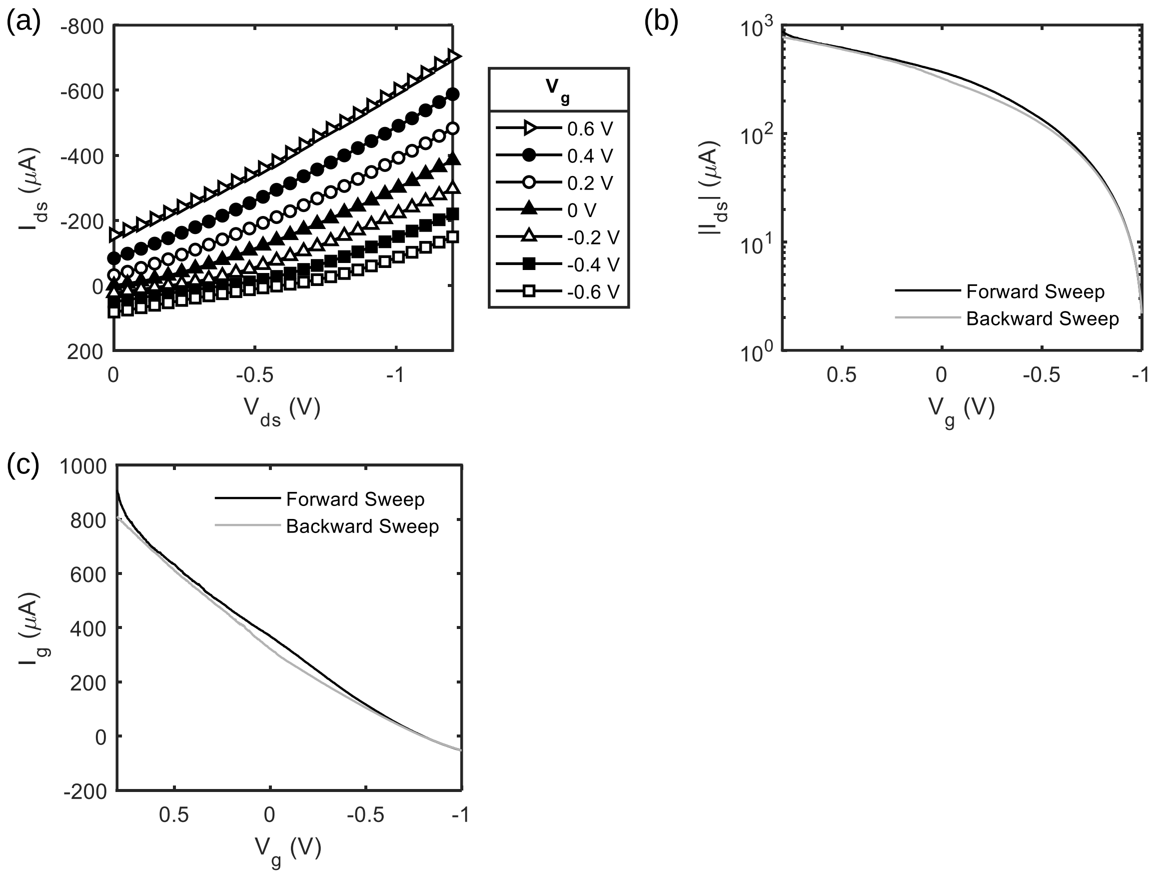

Figure S3 | Characteristics of a HIFET with DVS crosslinked PEDOT:PSS deposited in-situ as the gate electrode. (a) Output characteristics, (b) transfer recorded at V_{ds} = -1V, (c) gate current recorded during the transfer sweep.

Final devices

Figures S4, S5 and S7 show representative data for HIFETs using the standard, DVS crosslinked, and GOPS crosslinked gate electrodes. These represent devices with characteristics close to the average for each gate type. Sensing results for all tested devices are shown.

Standard gate electrode

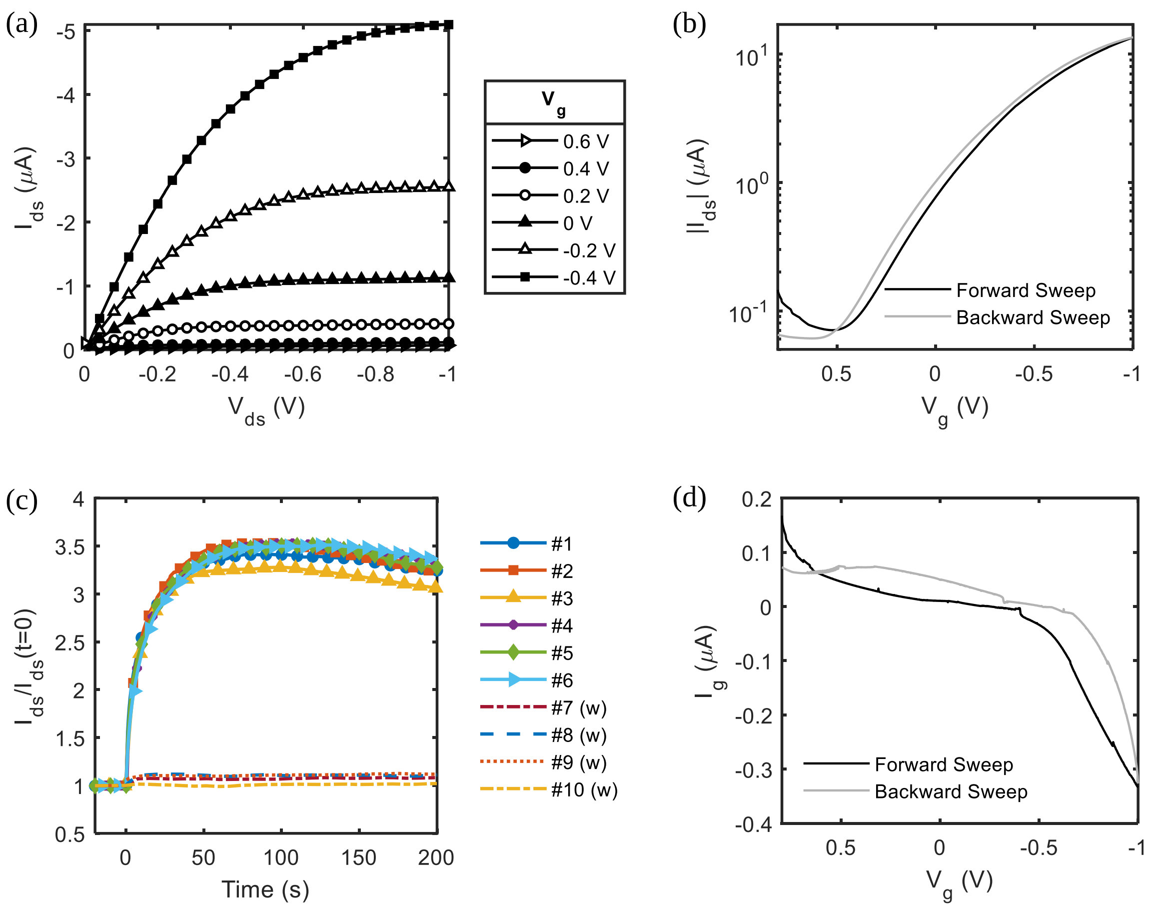

Figure S4 | Representative device characteristics for HIFETs with the standard gate electrode. (a) Output, (b) transfer (V_{ds} = -1 V), (c) I_{ds} modulation upon exposure to H_2O_2 (samples #1-6) and deionised H_2O (samples #7-10), and (d) gate current during the transfer sweep.

DVS crosslinked gate electrode

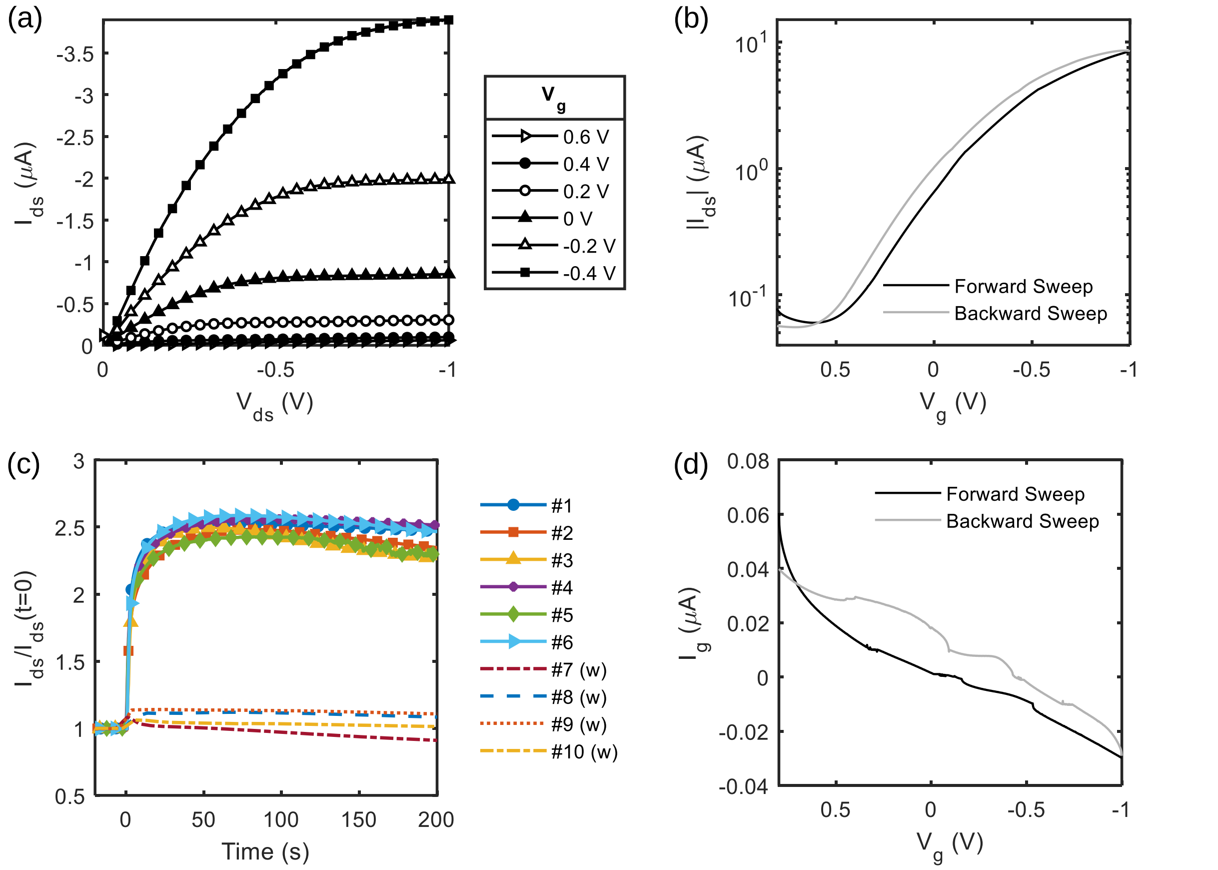

Figure S5 | Representative device characteristics for HIFETs with the standard gate electrode. (a) Output, (b) transfer (V_{ds} = -1 V), (c) I_{ds} modulation upon exposure to H_2O_2 (samples #1-6) and deionised H_2O (samples #7-10), and (d) gate current during the transfer sweep.

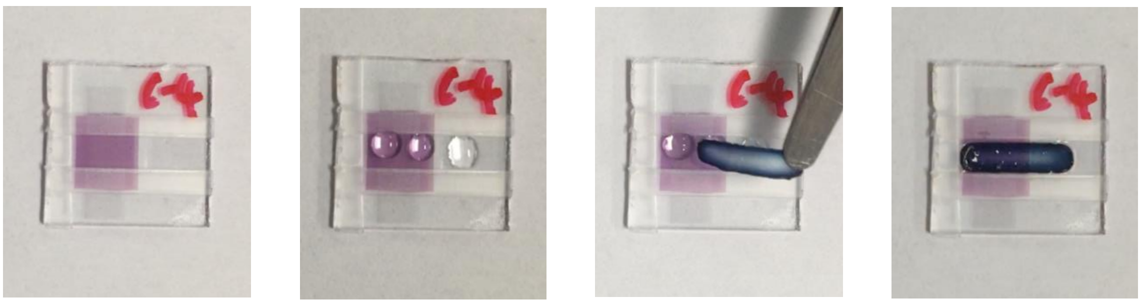

Figure S6 | Adhesion of free standing DVS crosslinked gate electrode using 0.1% GOPS. Photographs show the glass substrate, coated with P3HT and PVP, with strips of tape forming a guide for the gate position. The GOPS solution is then deposited, and the freestanding film is lowered into place.

GOPS crosslinked gate electrode

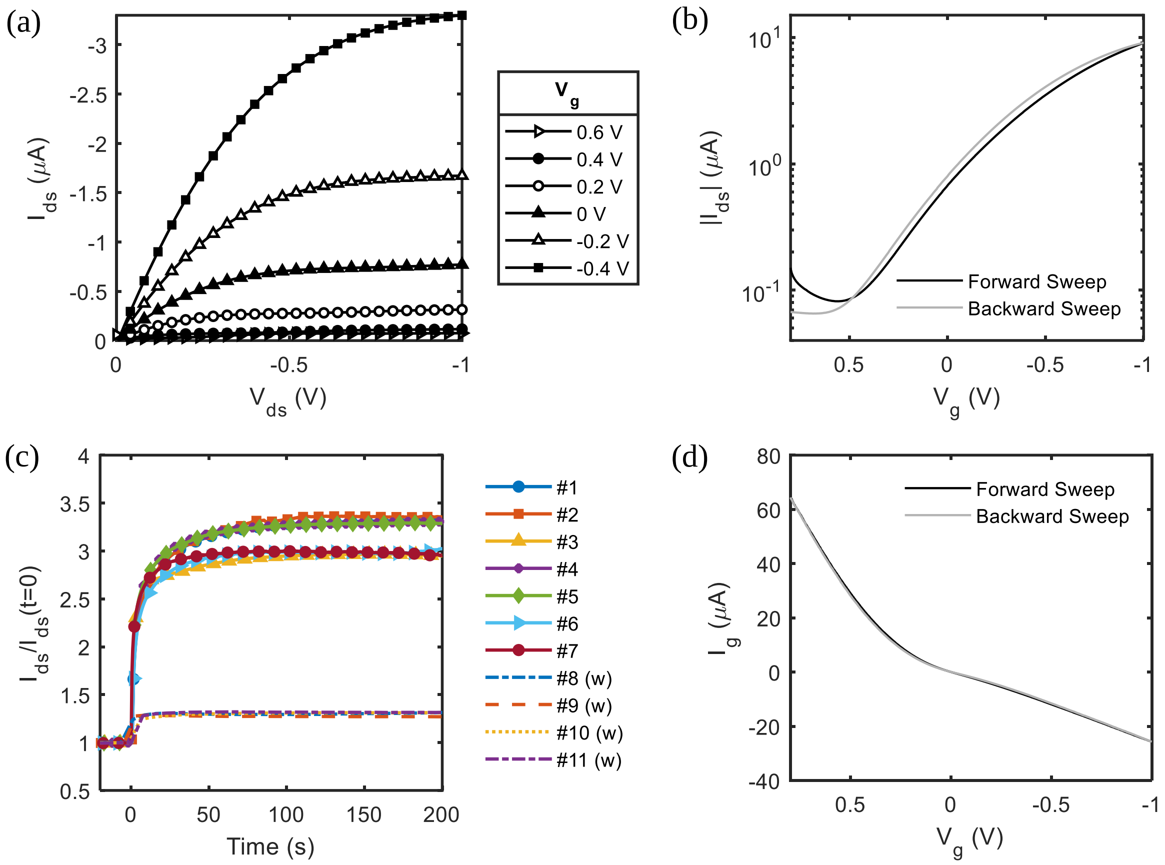

Figure S7 | Representative device characteristics for HIFETs with the GOPS crosslinked gate electrode. (a) Output, (b) transfer (V_{ds} = -1 V), (c) I_{ds} modulation upon exposure to H_2O_2 (samples #1-7) and deionised H_2O (samples #8-11), and (d) gate current during the transfer sweep.

Table S2 | Tabulated average figures of merit (with standard deviations) for HIFETs with different gate electrodes. ON and OFF currents are the maximum and minimum currents recorded during the backward transfer sweep, and ON/OFF is the ratio between the two. Transconductance is the maximum dI_{ds}/dV_g recorded during the transfer sweep, normalised by the channel width (3 mm). Turn-off voltage is the gate voltage at which I_{ds} is at a minimum during the backward transfer sweep.

Figure of merit	Standard	DVS crosslinked	GOPS crosslinked
ON/OFF	210 (±40)	150 (±20)	140 (±40)
ON current (μA)	-14 (±1)	-8.7 (±0.8)	-8.6 (±0.8)
OFF current (μA)	-0.07 (±0.02)	-0.06 (±0.01)	-0.06 (±0.01)
Transconductance (μS/mm)	5.8 (±0.4)	3.6 (±0.4)	3.3 (±0.3)
Turn-on voltage (V)	+0.61 (±0.02)	+0.70 (±0.04)	+0.67 (±0.02)
I_g at -1V (μA)	-0.4 (±0.1)	-0.1 (±0.1)	-8 (±10)
μ_{sat}×C (μA/V^2)	0.33 (±0.02)	0.23 (±0.03)	0.18 (±0.01)

Effect of analyte

Table S3 | Figures of merit for HIFETs with standard gate electrodes before and after depositing 5 μL of H_2O or H_2O_2.

Figure of merit	**Before**	**After H_2O**	**After H_2O_2**
ON/OFF	210 (±40)	230 (±20)	60 (±20)
ON current (μA)	-14 (±1)	-14.3 (±0.8)	-16.7 (±2)
OFF current (μA)	-0.07 (±0.02)	-0.06 (±0.01)	-0.30 (±0.06)
Transconductance (μS/mm)	5.8 (±0.4)	6.6 (±0.3)	6.5 (±0.8)
Turn-on voltage (V)	+0.61 (±0.02)	+0.6 (±0.1)	+0.65 (±0.02)
I_g at -1V (μA)	-0.4 (±0.1)	-0.73 (±0.13)	-1.09 (±0.06)
μ_{sat}×C (μA/V^2)	0.33 (±0.02)	0.34 (±0.02)	0.40 (±0.05)

Table S4 | Figures of merit for HIFETs with DVS crosslinked gate electrodes before and after depositing 5 μL of H_2O or H_2O_2.

Figure of merit	**Before**	**After H_2O**	**After H_2O_2**
ON/OFF	150 (±20)	140 (±90)	40 (±40)
ON current (μA)	-8.7 (±0.8)	-7.6 (±0.9)	-10 (±2)
OFF current (μA)	-0.06 (±0.01)	-0.07 (±0.4)	-1 (±1)
Transconductance (μS/mm)	3.6 (±0.4)	3.2 (±0.3)	3.4 (±0.6)
Turn-on voltage (V)	+0.70 (±0.04)	0.7 (±0.1)	0.6 (±0.3)
I_g at -1V (μA)	-0.1 (±0.1)	-0.19 (±0.05)	-0.6 (±0.3)
μ_{sat}×C (μA/V^2)	0.23 (±0.03)	0.24 (±0.03)	0.16 (±0.06)

Table S5 | Figures of merit for HIFETs with GOPS crosslinked gate electrodes before and after depositing 5 μL of H_2O or H_2O_2.

Figure of merit	**Before**	**After H_2O***	**After H_2O_2**
ON/OFF	140 (±40)	120 (±60)	3.2 (±0.5)
ON current (μA)	-8.6 (±0.8)	-11.0 (±0.9)	-13 (±1)
OFF current (μA)	-0.06 (±0.01)	-0.11 (±0.07)	-4.1 (±0.7)
Transconductance (μS/mm)	3.3 (±0.3)	5.1 (±0.2)	5.5 (±0.9)
Turn-on voltage (V)	+0.67 (±0.02)	0.43 (±0.04)	-0.06 (±0.08)
I_g at -1V (μA)	-8 (±10)	-0.8 (±0.1)	-20 (±20)
μ_{sat}×C (μA/V^2)	0.18 (±0.01)	0.27 (±0.03)	0.12 (±0.04)

**Note that only 2 good devices were available for the 'after H_2O' test, and so this data should not be heavily relied upon. The apparent drop in gate current is simply because those two devices happened to begin with low gate leakage.*