Supporting Information

Printed oxygen gas sensor using Copper-DTDTPA solid electrolyte

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TABLE S1 Summary of publications and patents related to solid state oxygen sensors

S. No	Publication/ Patent	Electrode/ Electrolyte	Sensor parameters/ Method
1	Yao et al., 2016[4]	SNDC-AO multilayered structure	Response time of 0.4 s, recovery time 0.1 s, maximum output voltage 0.4 V at 500°C
2	Dunst et al., 2014[5]	Pt-Ni-NiO/ YSZ	Maximum OCV of 1.4 V at 500°C
3	Kalyakin et al. 2020[6]	0.91ZrO_2 + 0.09 Y_2O_3 solid electrolyte	Sensor response time at 500 °C does not exceed the 60 s.
4	Patent-US5827415A	Zirconia based Solid electrolyte	Operational above 300 °C.
5	Lee et al., 2020[2]	Poly(vinylidene fluoride-co-hexafluoropropylene)-ionic liquid mixtures	Thin film based sensing, amperometric sensors, response time 10 s (extremely fast) due to use of thin films
6	Hussain et. al., 2018[3]	Microelectrode arrays with ionic liquids	Amperometric sensing, proof of the concept established.

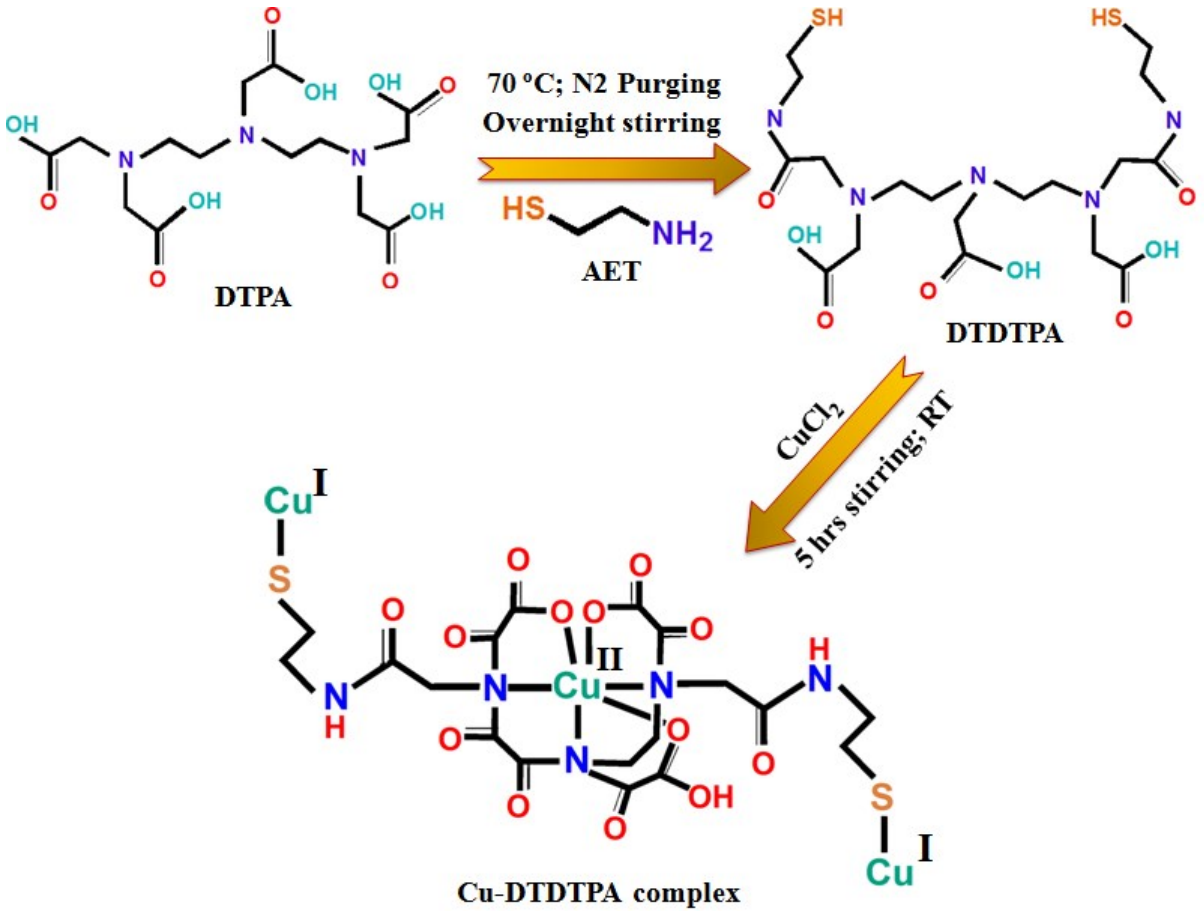


Figure S1. Schematic of synthesis procedure for Cu-DTDTPA complex

Methodology for material synthesis and sensor fabrication

The oxygen sensor consists of a grade 1 filter paper adsorbed with Cu-DTDTPA complex with 3-D printed Ag/AgCl electrodes in interdigited configuration.DTDTPA was synthesized following a previously reported procedure[7] that involves conjugation of diethylenetriaminepentacetic acid bis-anhydride (DTPA-BA) with 2-aminoethanethiol (AET) through amide linkage. 1 g (5.6×10^{-3} mol) of DTPA-BA, (supplier- Sigma Aldrich, USA) was dissolved in 20 mL of dimethylformamide (DMF), (supplier- Merck, Germany) and heated at 70 ºC in an inert environment created by purging nitrogen gas (N_2). In another flask, 0.7 g (1.23×10^{-2} mol) of AET (supplier- Himedia) was dissolved in a solution of 15 ml of DMF and 0.87 mL of triethylamine. This solution was added to the first reaction flask and stirred at 70 °C overnight under N_2 environment. The solution was cooled to room temperature and placed in ice bath. A white precipitate of triethylamine hydrochloride ($NEt_3 \cdot HCl$) formed was filtered out and filtrate was concentrated at low pressure. Next, chloroform was added to the concentrated product forming a white precipitate. The resultant precipitate was filtered and

washed with 50 ml chloroform followed by drying under vacuum to yield a white colored substance. To prepare Cu-DTDTPA complex, 6 mM solution of DTDTPA was prepared by dissolving 3.0 mg of DTDTPA in 1.0 mL de-ionised water. 18 mM solution of $CuCl_2$ (supplier-Himedia) (3 mg $CuCl_2$ dissolved in 1.0 ml de-ionised water) was added to DTDTPA and stirred overnight at room temperature. A light blue colored solution was formed in the process.

A grade-3 laboratory filter paper of size 4 cm X 3 cm was thoroughly washed in ethanol and was dipped in Cu-DTDTPA for 24 hours. The filter paper was then dried in an oven at 60°C for 12 hours. Interdigited electrodes were then printed over the filter paper using a 3-D printing conductive ink printer (make: Voltera, V-One) with anode consisting of conductive silver ink (type- Jazzy Juzak, make- Voltera) and cathode consisting of conductive silver chloride ink (make- Sigma Aldrich). The internal nozzle diameter used for printing Ag and AgCl was 225 µm and was selected after repeated experimental trials by visually inspecting the print quality. The printed ink layer thickness was fixed to 0.4 mm and was printed in 4 passes by the 3-D printer. The consecutive digits and the digit thickness of the interdigited electrodes were set to 1 mm. The printed filter paper containing Cu-DTDTPA was heated at ~100°C for 1 hour for drying the conductive ink in the integrated oven supplied with the 3-D printer.

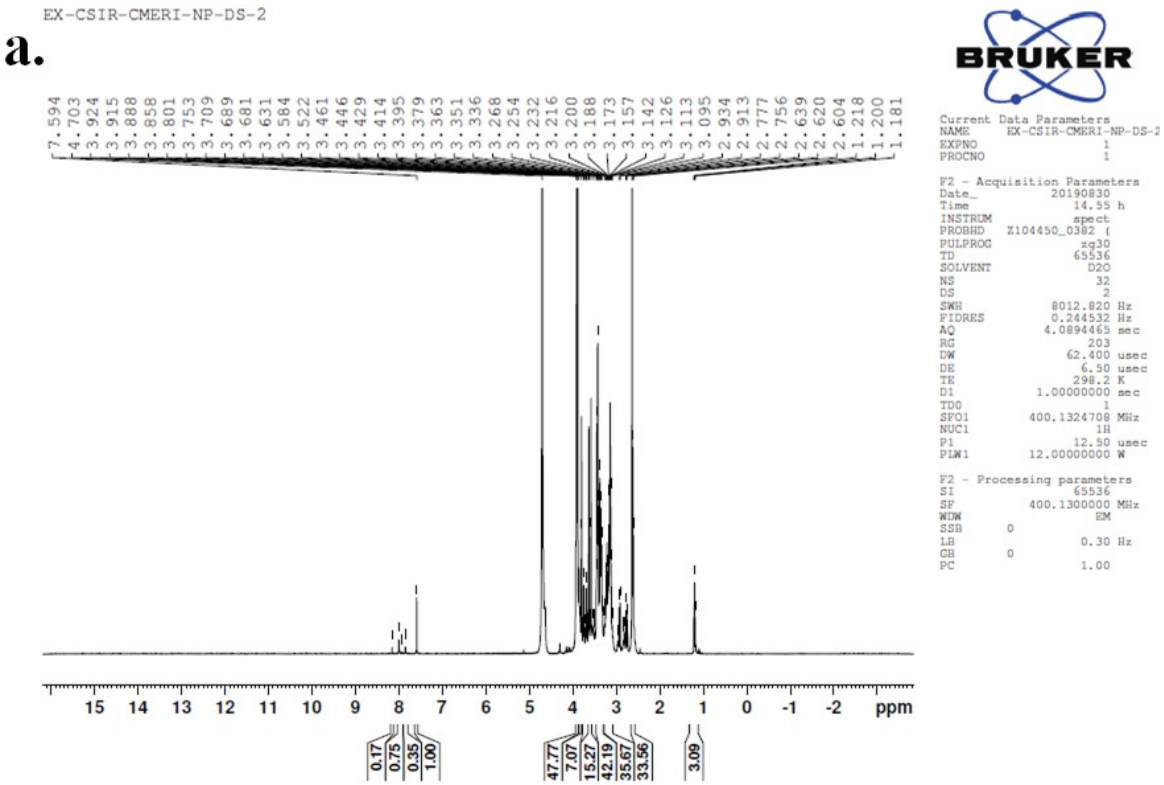


Figure S2. (a). 1H NMR spectra of DTDTPA (b). Liquid chromatography-mass spectra (LC-MS) of DTDTPA . m/z 512.7 $[M+H]^+$; Inset shows the chemical structure and molecular weight of DTDTPA (theoretically calculated MW: 511 g mol^{-1}).

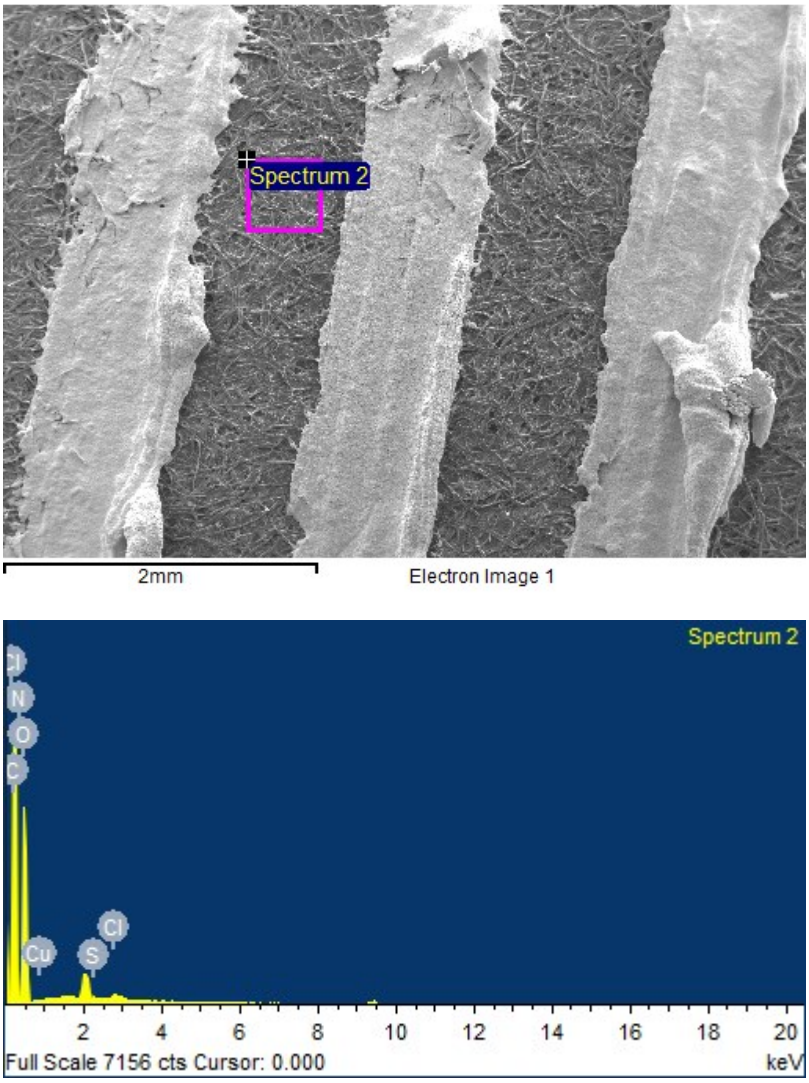


Figure S3. EDX results for the sensor portion wherein filter paper is adsorbed with Cu-DTDTPA. Prominent peaks of Cu, Cl, N, O, C and S could be found in the results

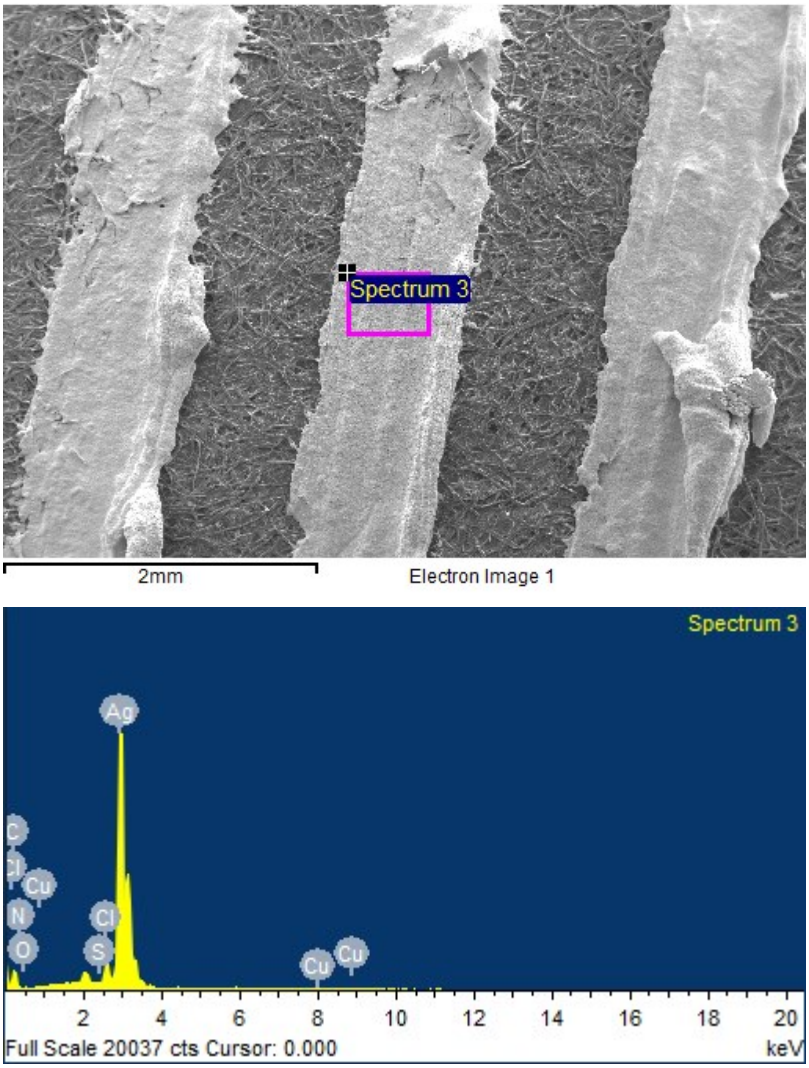


Figure S4. EDX results for the sensor portion wherein Ag paste is printed over filter paper adsorbed with Cu-DTDTPA. Prominent peaks of Ag, Cu, Cl, N, O, C and S could be found in the results.

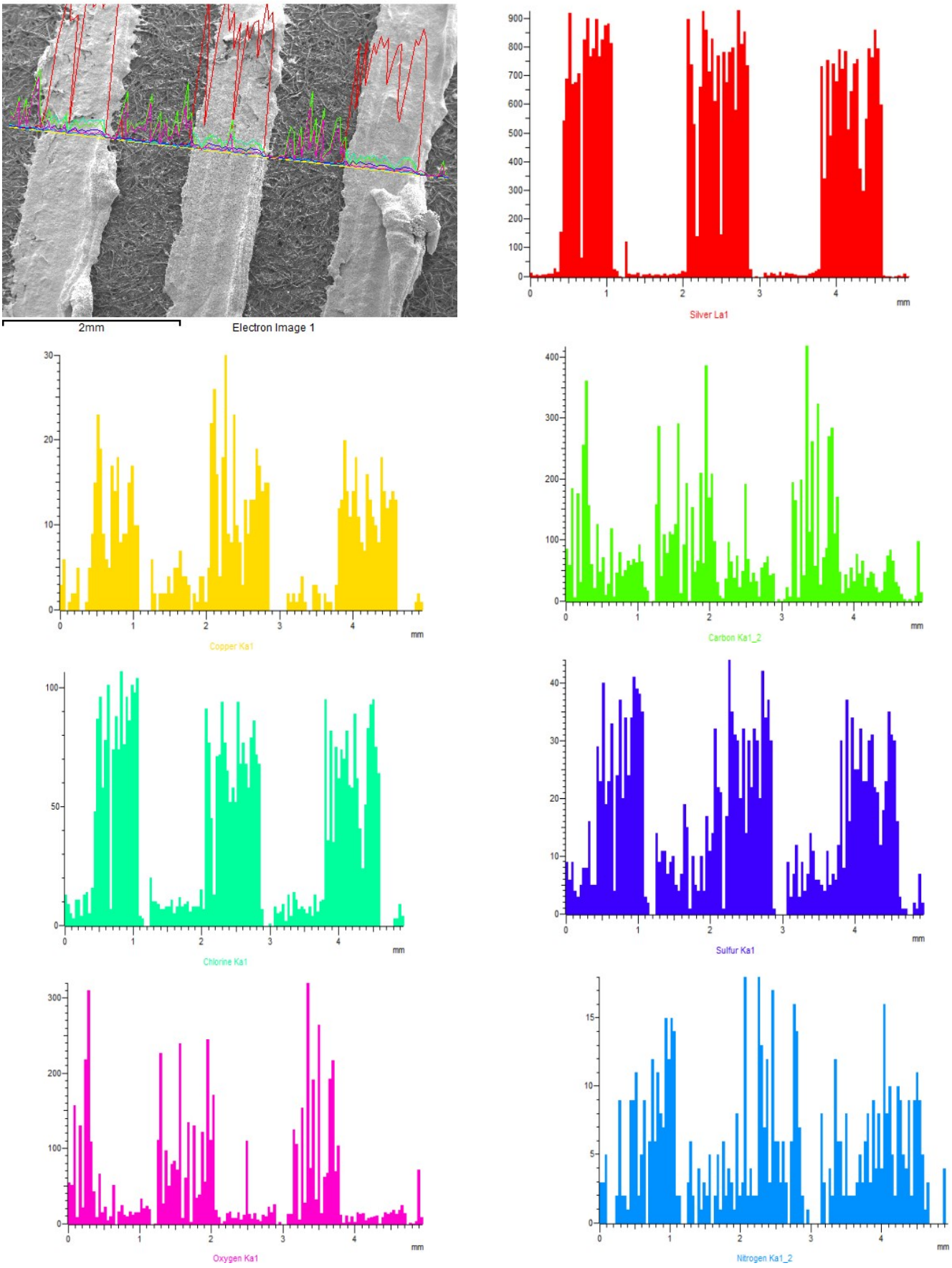
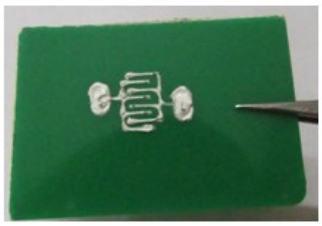
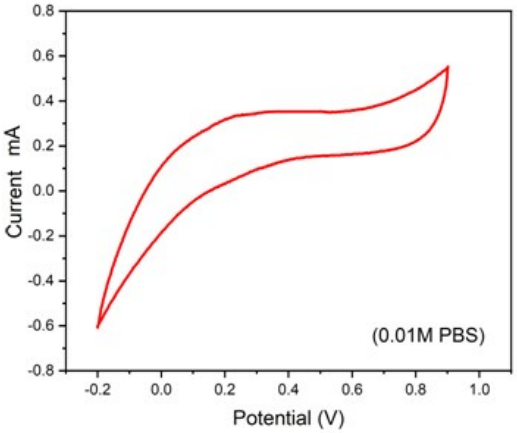


Figure S5. EDX analysis map showing the location of various elements in the fabricated sensor. The map confirms that Ag printing were precise since their locations are only at the printed regions.



Ag/ AgCl printed interdigited electrode printed over FR4 substrate



Cyclic voltammetry of electrodes in 0.01M Phosphate buffer solution

Figure S6. Ag/ AgCl electrodes printed over FR4 substrate and the cyclic voltammetry plot of the electrodes in 0.01 M Phosphate buffer solution showing absence of peaks confirming that the electrodes do not take part in reaction.

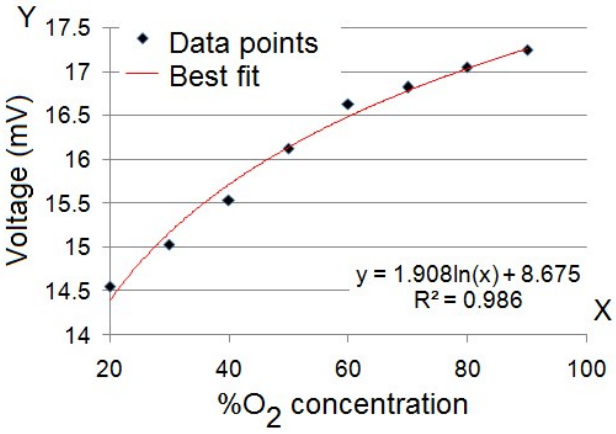


Figure S7. Logarithmic fitted curve for the sensor response at 25°C

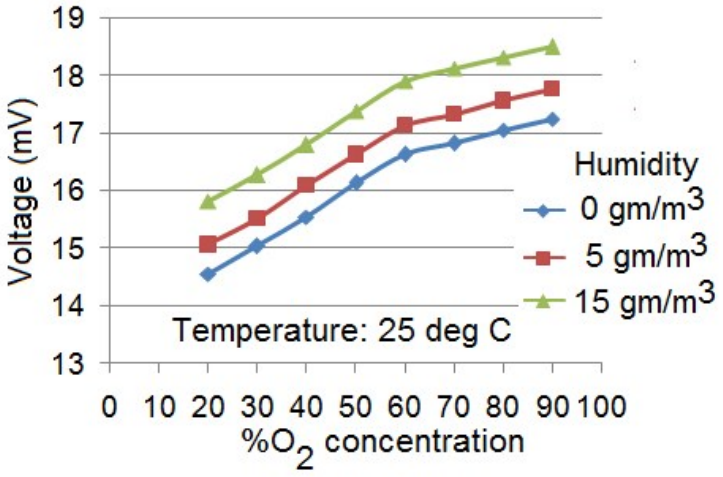


Figure S8. Response of the developed sensor with varying absolute humidity in gas chamber at 25 °C temperature

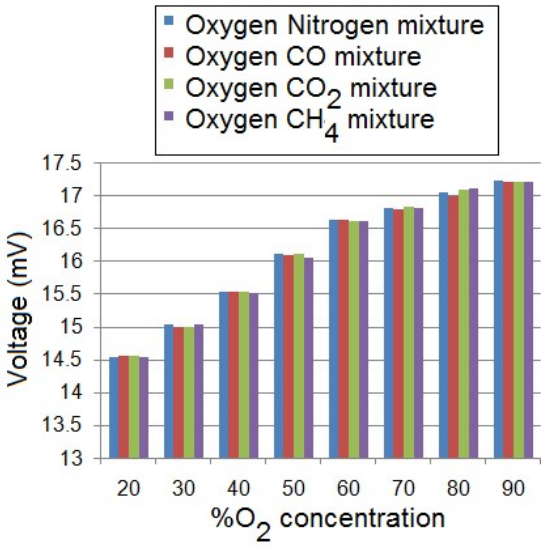


Figure S9. Response of the developed sensor with varying O_2 concentration mixed with remaining amount of other gases such as Nitrogen, CO, CO_2 and CH_4. (For eg. 20% O_2 concentration in the plot refers to a mixture of 20 % O_2 with 80% Nitrogen gas- Blue colour bar, 20 % O_2 with 80% CO- Brown colour bar, 20 % O_2 with 80% CO_2- Green colour bar, 20 % O_2 with 80% CH_4- Purple colour bar)