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MOF Based Flexible, Low-Cost Chemiresistive Device as a Respiration Sensor for Sleep Apnea Diagnostics

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EXPERIMENTAL DETAILS

Materials Required

Cupric Nitrate Trihydrate [$Cu(NO_3)_2.3H_2O$] extrapure, N,N′- dimethyl formamide (DMF), methanol were purchased from SRL, 1,3,5- benzene tricarboxylic acid (BTC) was purchased from TCI chemicals. All the reagents and solvents were used as such without additional purification.

Synthesis Procedure

$Cu_3(BTC)_2$, (HKUST-1)] was synthesized according to the reported procedure[1] with slight modifications. $Cu(NO_3)_2.3H_2O$ (1.4mmol) and 1,3,5- benzene tricarboxylic acid (0.8 mmol) were dissolved in 10 ml of water, ethanol and dmf mixture in the ratio 2:1:1. The solution was sonicated for about 10 minutes until the reagents were dissolved completely. The vial was then placed in the oven at 373 K. The vial was removed from the oven after 12 hrs and cooled to room temperature. The blue crystals thus obtained were washed thoroughly with DMF and ethanol. The resulting product was then dried at 343 K for further characterization.

Powder X-ray Diffraction (PXRD)

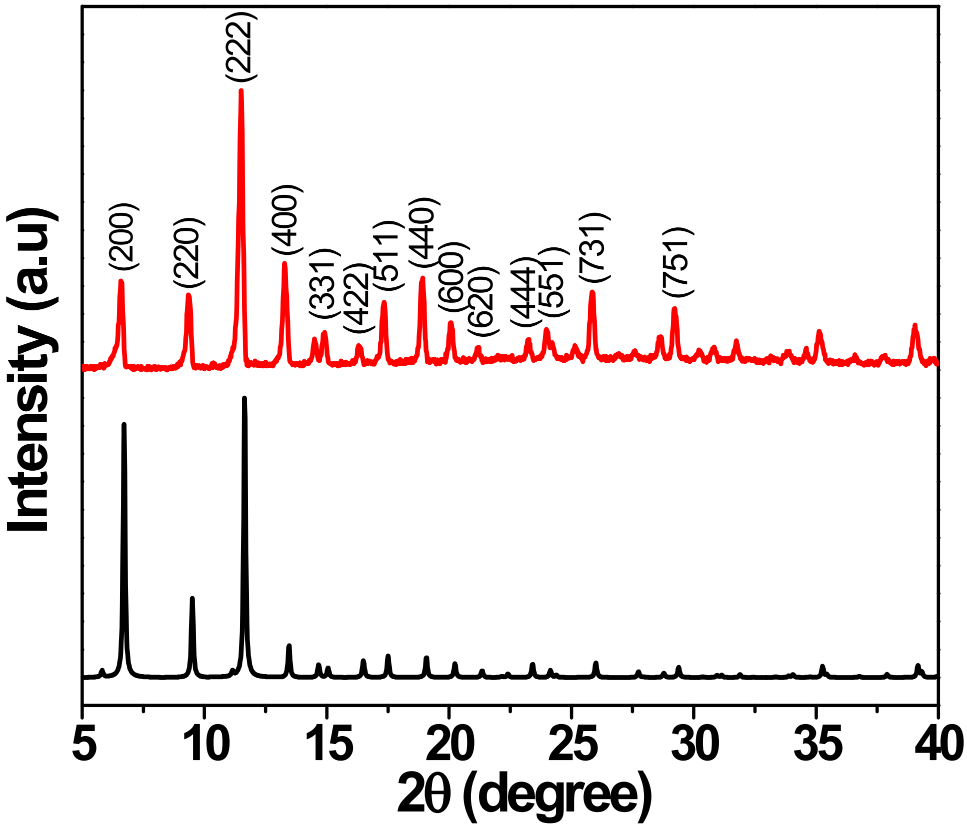


Fig. S1. Comparison of the experimental (red) and calculated (black) PXRD patterns of HKUST-1.

Thermo Gravimetric Analysis (TGA)

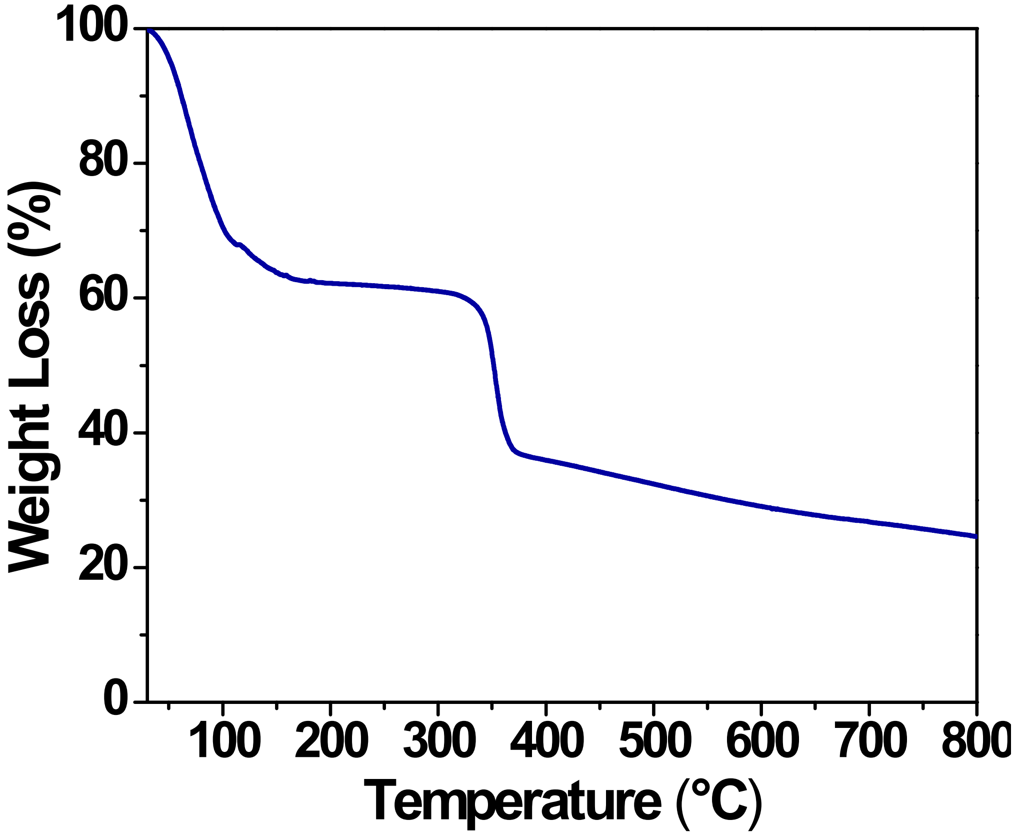


Fig. S2. TGA profile of as-synthesized HKUST-1 crystals.

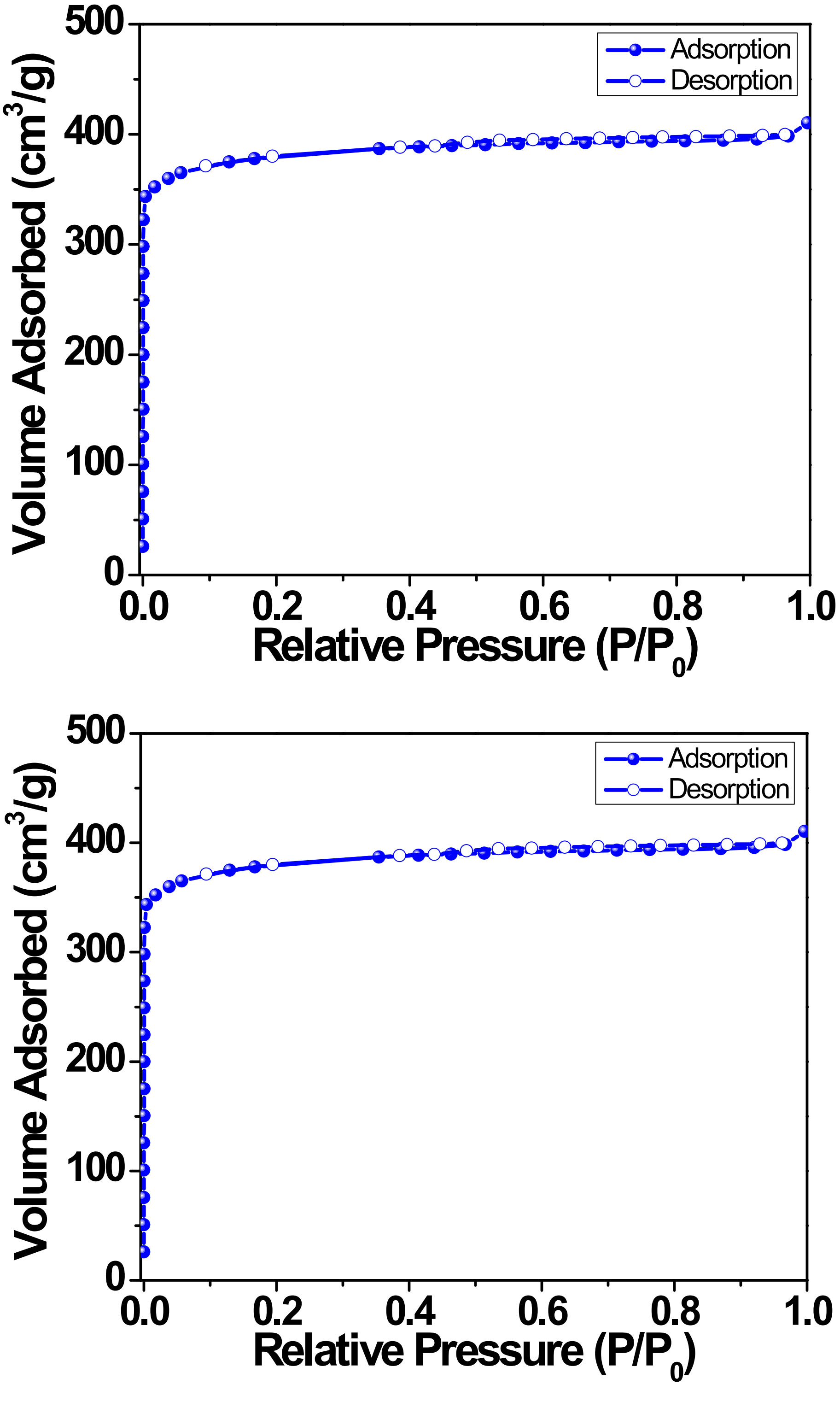


Fig. S3. N_2 sorption isotherm for the (a) pristine and (b) grinded HKUST-1 samples.

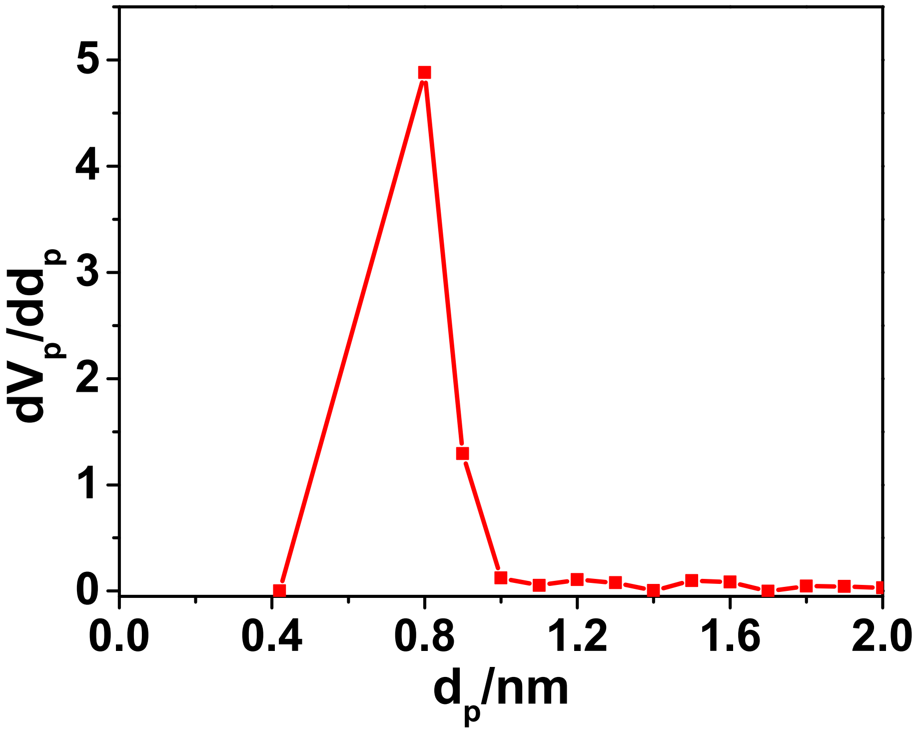


Fig. S4. Pore size distribution of activated HKUST-1 MOF.

Field Emission Scanning Electron Microscopy (FE-SEM)

The SEM images of the as-synthesized HKUST-1 MOF depict octahedral crystals with sharp edges with size ranging from **7** μm – 30 μm. The SEM images of MoS_2 on support and HKUST-1 drop casted on MoS_2 support depict uniform coating (**Fig. S5)**.

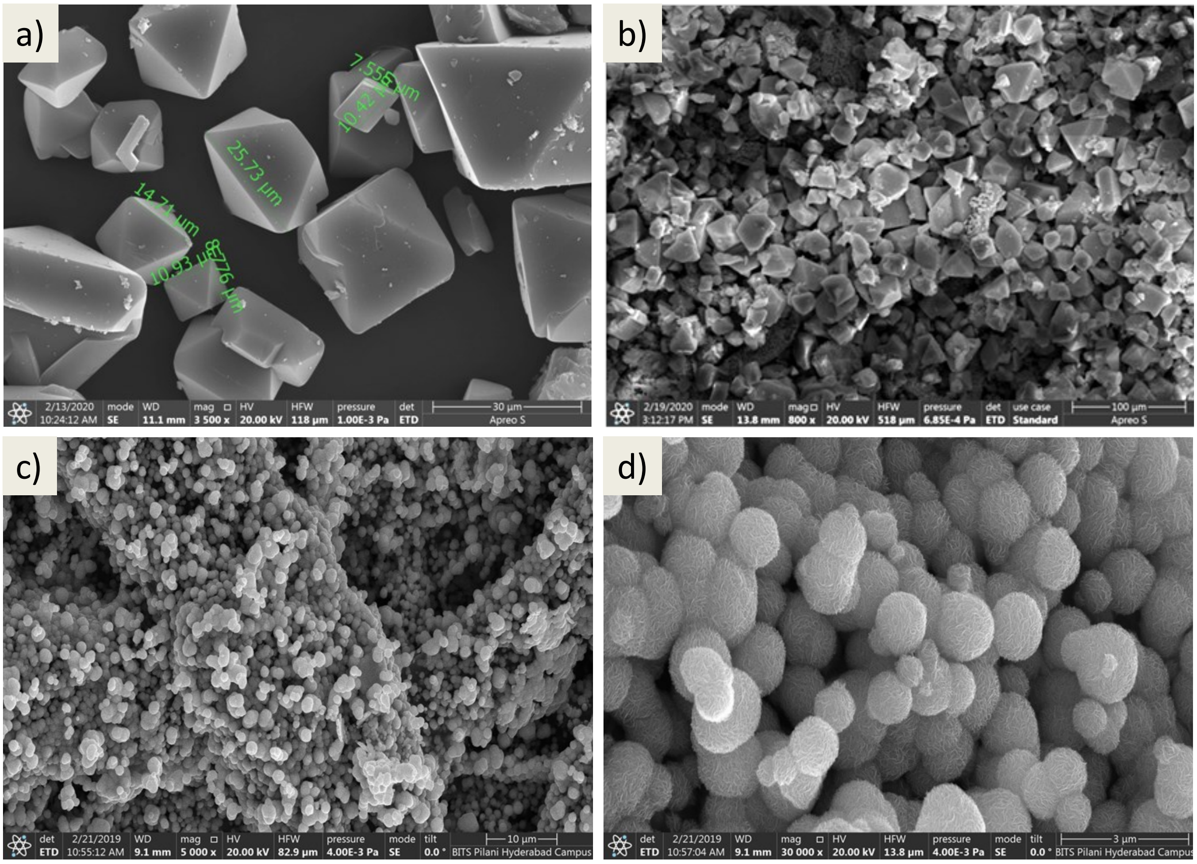


Fig. S5. SEM images of (a) HKUST-1 MOF single crystals (b) HKUST-1 MOF on MoS_2 (c) MoS_2 on cellulose paper and (d) MoS_2 on Cellulose paper (Magnified view).

Element	Weight%	Atomic%
C	44.07	61.01
O	31.33	32.56
Cu	24.60	6.44
Totals	100.00	

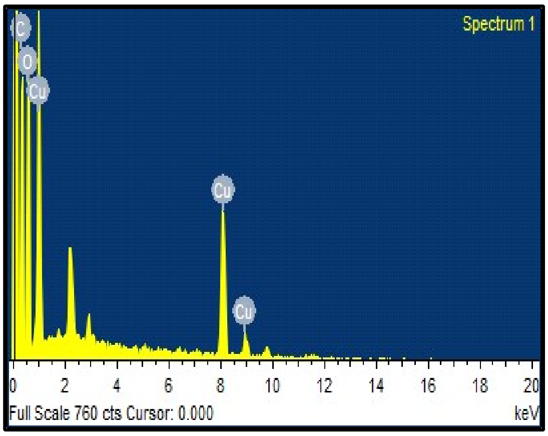


Fig. S6. EDX spectrum and elemental data of Cu-BTC MOF.

X-ray Photoelectron Spectroscopy (XPS)

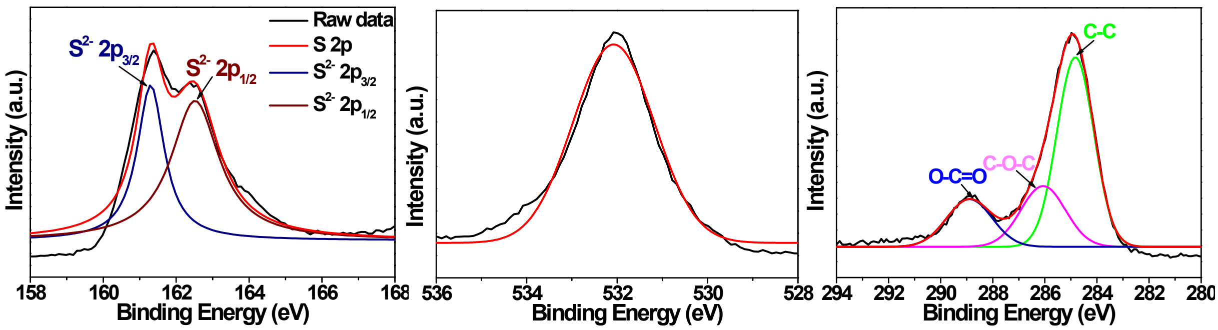


Fig. S7. XPS spectra of HKUST-1 MOF on MoS_2 showing binding energies for a) S 2p, b) O 1s and c) C1s.

Breath sensing experiments

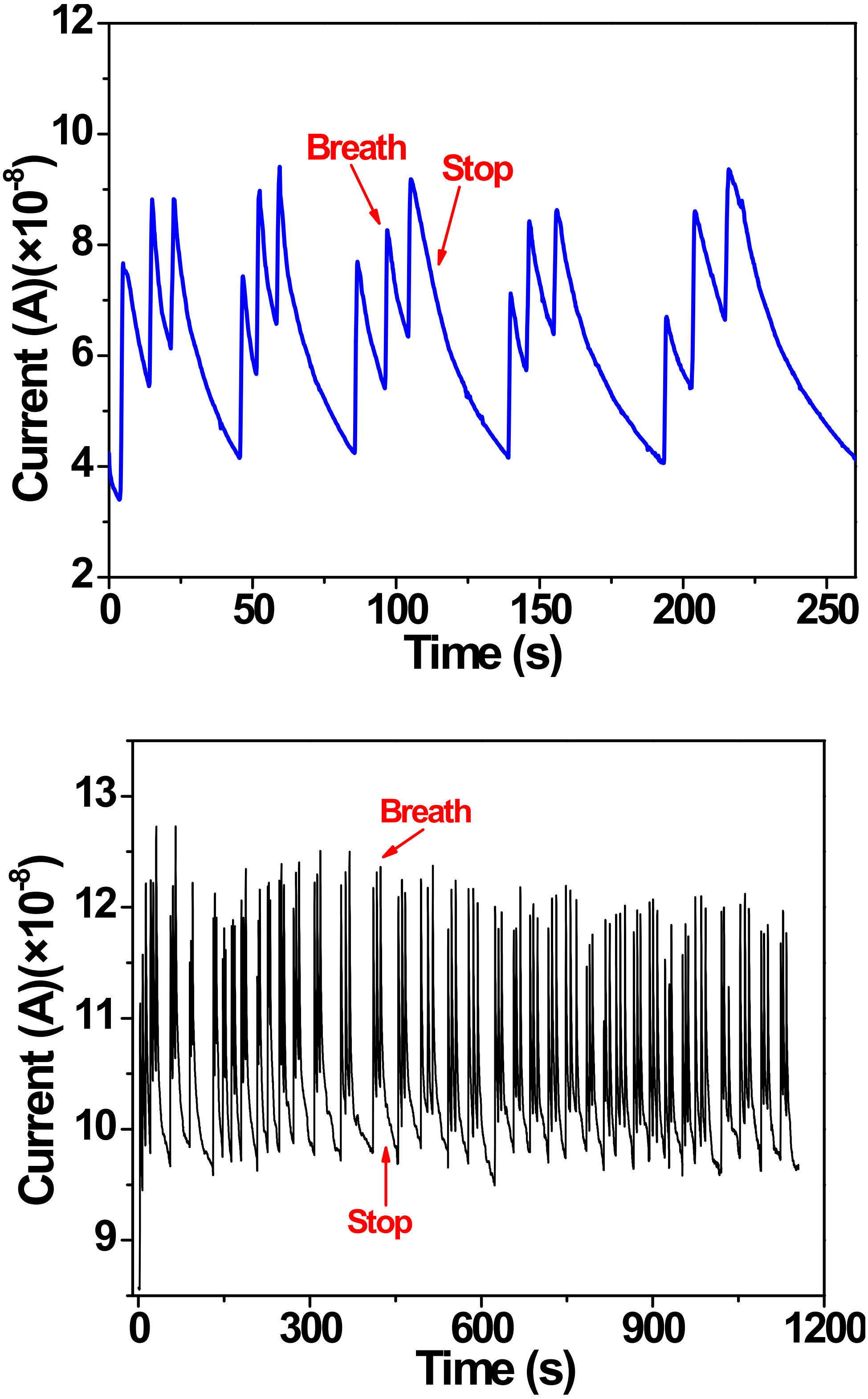


Fig. S8. Breath sensing experiments showing five breath cycles of three breaths each (top), and three breath iterative breathing pattern for around 1000 sec (bottom).

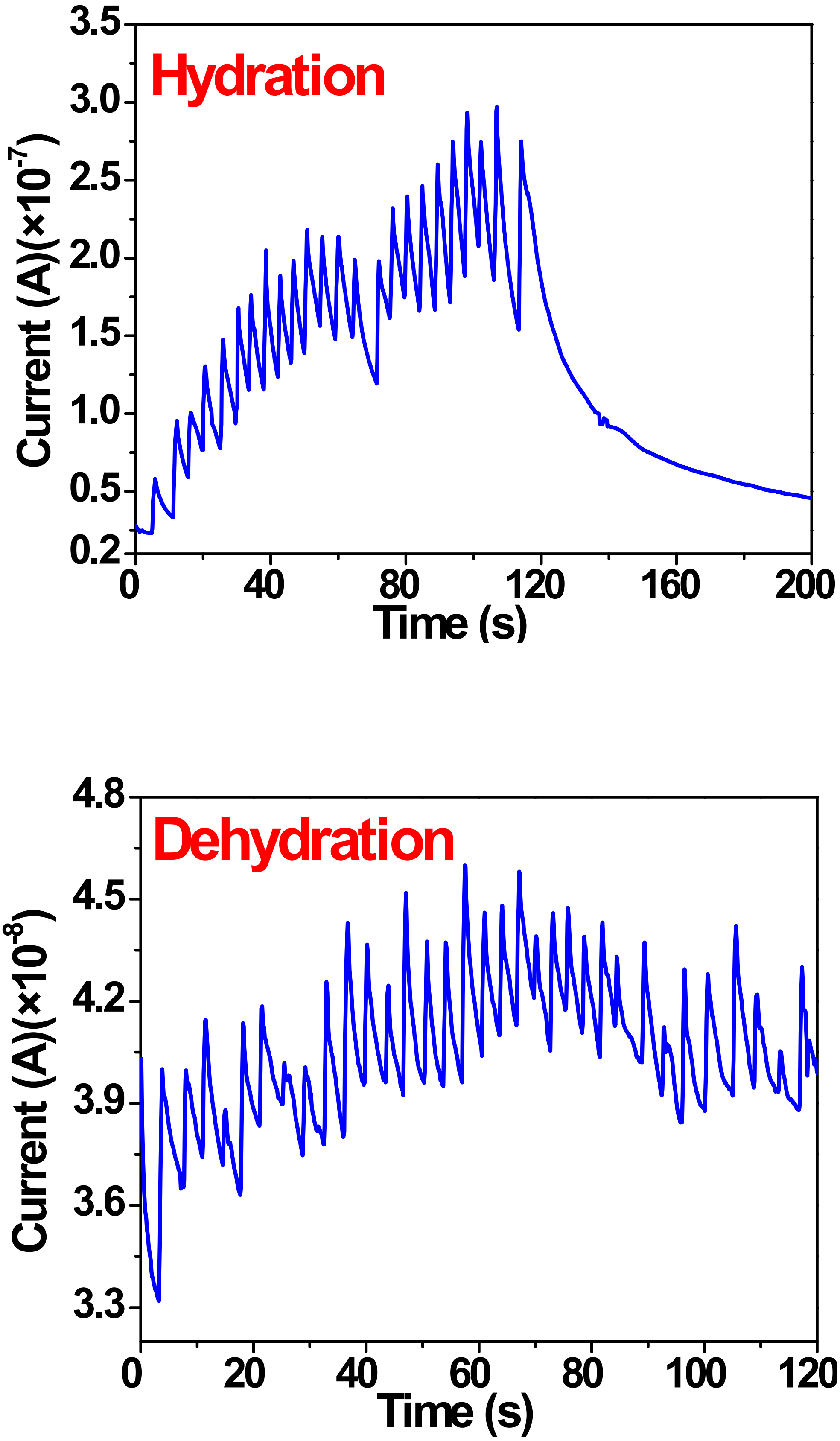


Fig. S9. Breath sensing experiments for hydrated (top), and dehydrated (bottom) breaths.

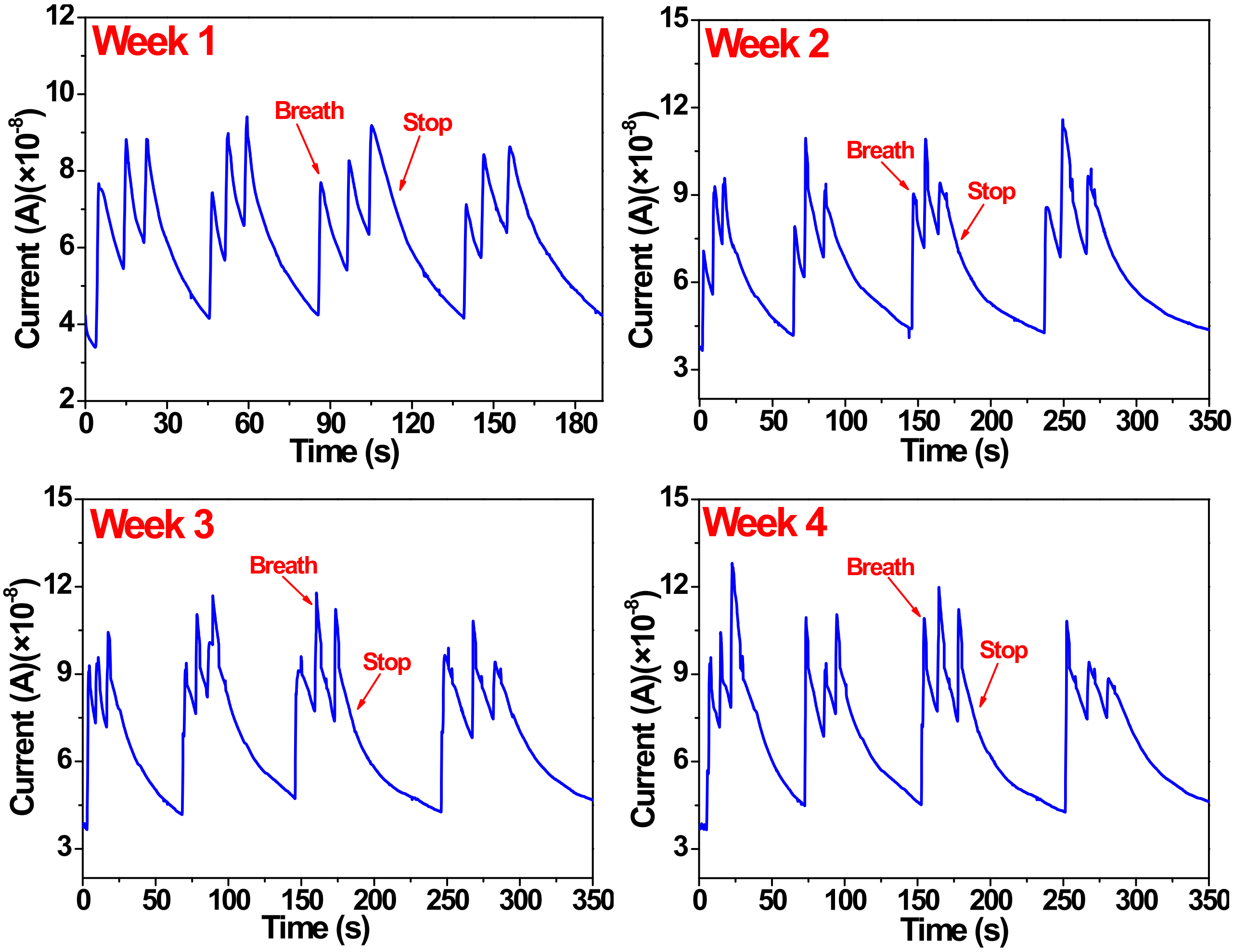


Fig. S10. Breath sensing experiments showing stability of HKUST-1-MoS_2 sensor over a period of 4 weeks.

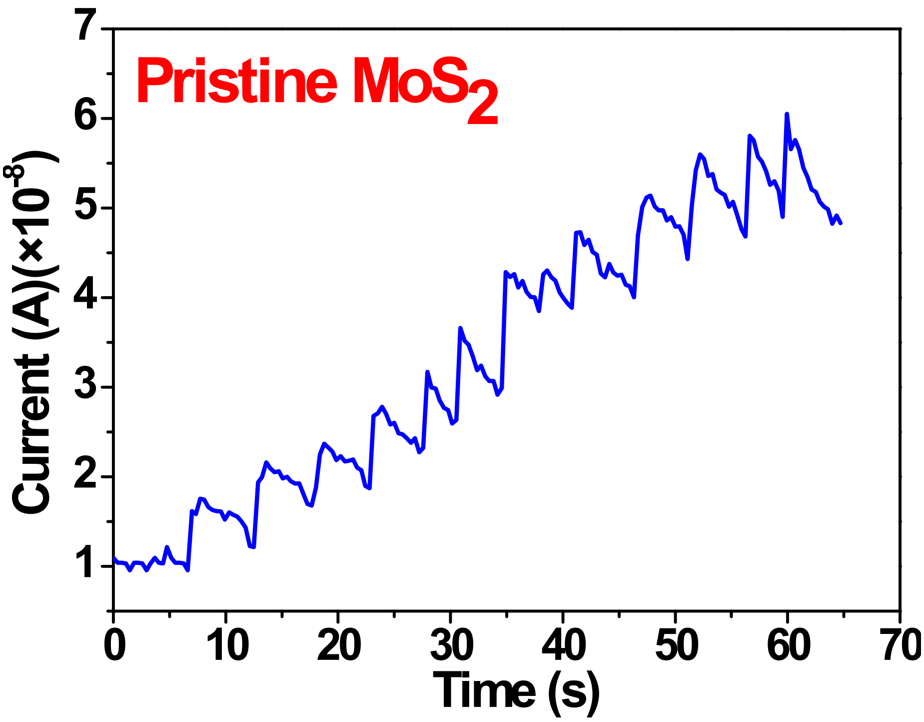


Fig. S11. Breath sensing experiments for pristine MoS_2.

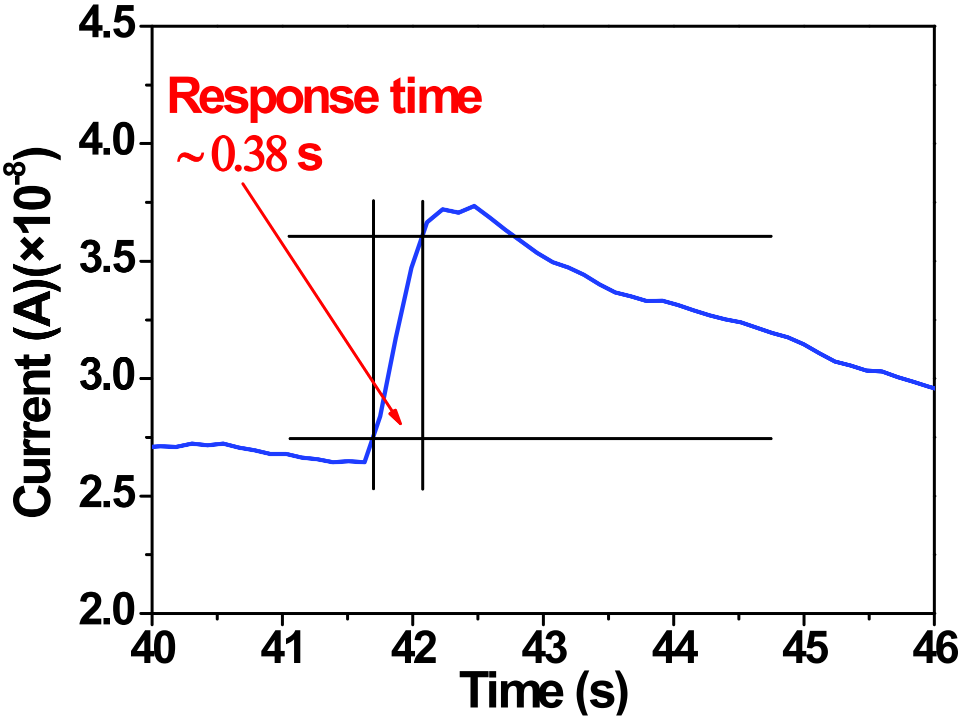


Fig. S12. Response time of HKUST-1-MoS_2 breath sensor.

Table S1. A comparison of the response time and support used for various breath sensor materials reported in the literature with the MOF sensor in the present study.

Sensor	Support	Material Type	Flexible	Response time (s)	Smartphone Integration	Reference
Al_2O_3	SiO_2	Metal Oxide	No	0.3	No	[2]
Carbon nanocoil	Liquid crystal polymer	CNC	Yes	1.6	No	[3]
Polyimide	Silicon	Polymer	No	1	No	[4]
Polyelectrolyte (PMDS)	Ceramic plate	Polymer	No	0.29	No	[5]
Polyester tape	Paper	Polyester	Yes	472	No	[6]
PEDOT:PSS Nanowires	PET	Nanowires	Yes	0.63	Yes	[7]
Zeolite Clinoptilolite	---	Zeolite	No	---	No	[8]
WS_2 film	PDMS	2D Semiconductor	Yes	5	No	[9]
MoS_2/Ag films	SiO_2/Si	MoS_2 Composite	No	1.5	No	[10]
HKUST-1/MoS_2	Cellulose Paper	MOF	Yes	**0.38**	Yes	**This work**

Smartphone Prototype

The $MOF\text{-}MoS_2$ device was fabricated as shown in the following figure. The MOF coated device was imbedded inside the mask and the signals were recorded with the help of a smartphone device.

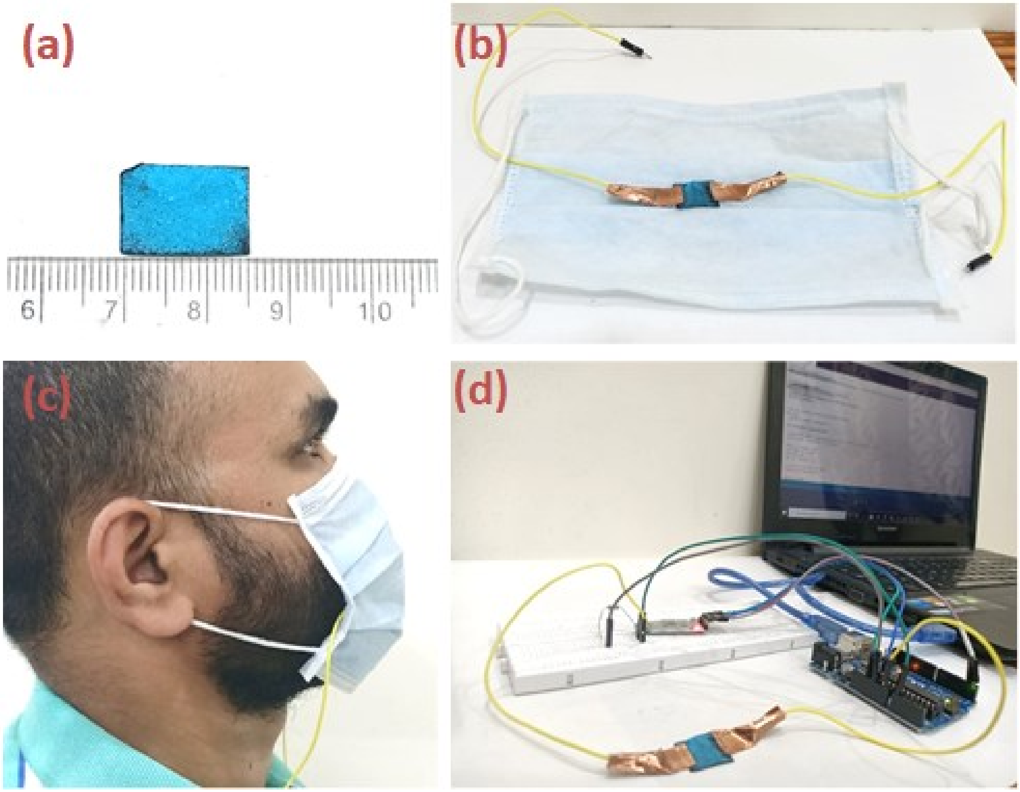


Fig. S13. Fabrication of the $MOF\text{-}MoS_2$ breath sensor. (a) MOF coated on MoS_2 paper support, (b) fabricated device, (c) fabricated device imbedded inside the mask and (d) connection of the device with the signal processing unit for android based smartphone prototype.

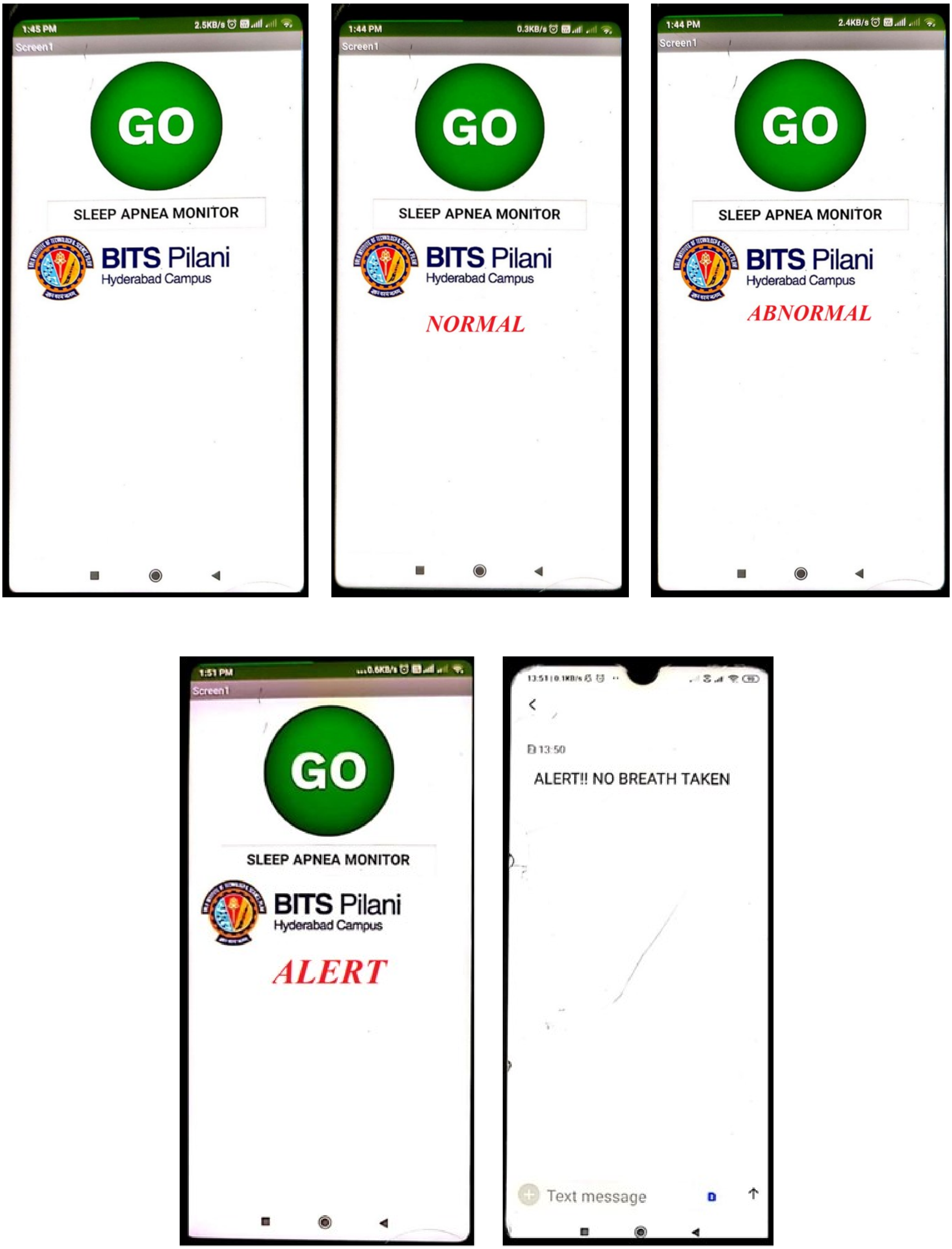


Fig. S14: Different types of signals shown by the android app; normal and abnormal (top) and alert (bottom).

Details of the Android Application

This app aims to showcase a practical functionality of the fabricated device. It can be seen from the attached graphs that there is a marked drop in the resistance as the device is exposed to moisture. This property of the material is exploited in building this app.

An Arduino based setup is used to make this work. Using a potential divider circuit, the resistance of the device is measured. The average of the first five readings is taken as a reference. Once the device is in use, the very first reading (R_0) will be compared against this reference value (R_f). The percentage change between two readings is measured as the 'change' integer.

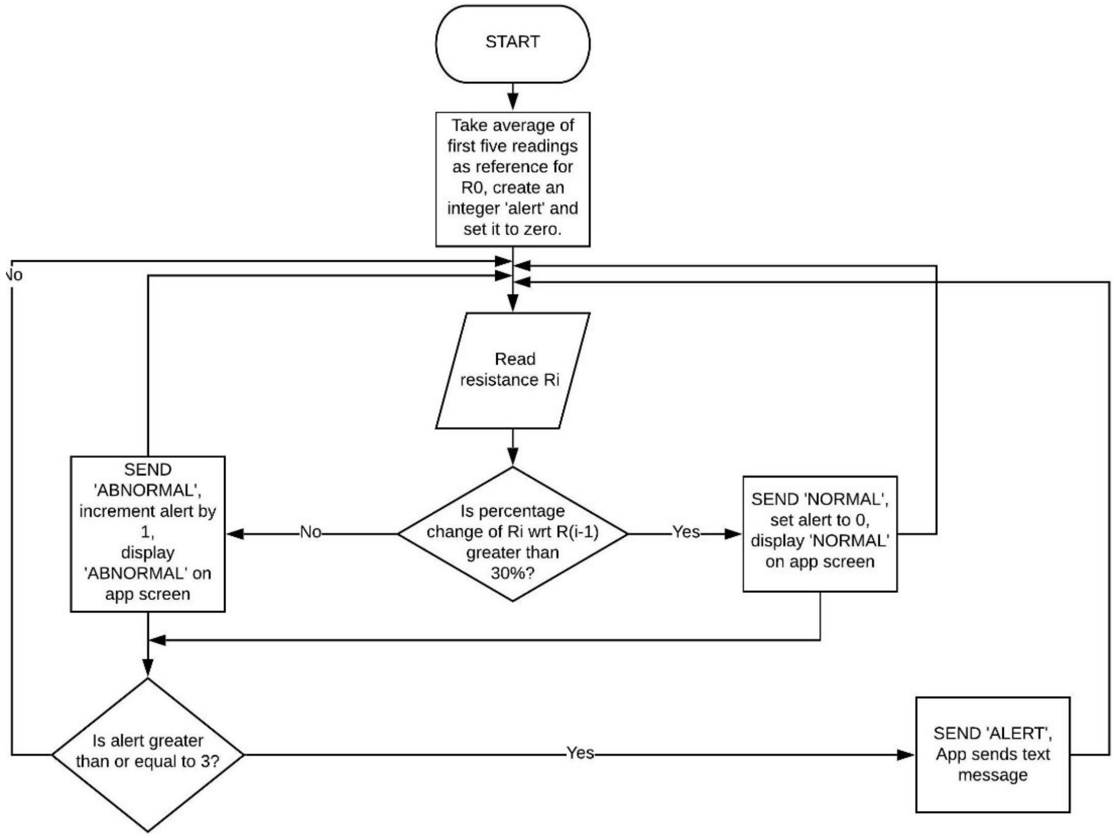
$$change = \frac{R_{i-1} - R_i}{R_{i-1}} \times 100$$

If this change is greater than 30%, there has been a drop in the resistance, i.e., the user has taken a breath, which exposed the device to moisture. When this change is noticed, the Arduino transmits a **'NORMAL'** message via Bluetooth, which can be received on a mobile phone app. We also have an integer variable 'alert', which will be set to zero every time breath is taken.

If change is lesser than 30%, there has not been a change in resistance for a certain period of time. This means there was no breath taken, and **'ABNORMAL'** message is transmitted by Arduino via Bluetooth. Also, after this event, integer variable 'alert' is incremented.

When 'alert' is greater than or equal to three, it means that there has been no breath taken by the user for three consecutive readings (three consecutive ABNORMAL signals)- This prompts Arduino to transmit an **'ALERT'** message via Bluetooth. This will trigger the app to send an SMS to the user's family, notifying them that there has been no breath taken for a while.

The flowchart of the algorithm for this function is as below:



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